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A REVIEW OF THE TOXICOLOGY OF COLORED CHEMICAL SMOKES AND COLORED SMOKE DYES

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This report is a review of the inhalation (total-body-exposure) studies performed by this laboratory during 1966 with the M18 series of colored smokes. The acute toxicities of the smokes, the times to death, and the gross signs are compared. A literature survey and toxicological evaluation of the various dyes in the violet, green, and red smoke mixtures are included. Studies necessary for definition of the hazards incident to the use of the dye components in manufacturing and military operations as well as knowledge gaps are described.

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PREFACE

The work described in this report was authorized under Task 1C522301A079, Non-Defense Medical Aspects of Chemical Agents, Toxicity Studies in Support of Research Tasks and Programs. All phases of the investigations described herein and conducted in this laboratory were conducted during 1966.

In conducting the research described in this report, the investigators adhered to the "Guide for the Care and Use of Laboratory Animals," as promulgated by the Committee on Revision of the Guide for Laboratory Animals Facilities and Care of the Institute of Laboratory Animal Resources–National Research Council.

CONTENTS

A REVIEW OF THE TOXICOLOGY OF COLORED CHEMICAL SMOKES AND COLORED SMOKE DYES

I. INTRODUCTION.

At the present time there are four standard colored signaling smokes. red. yellow, green, and violet. Operationally, they can be used to identify friendly units, to control the laying and lifting of artillery, mortar, and small arms fire, to identify targets, and to coordinate the fire and maneuver of combat arms engaged in local assault operations. Four characteristics of signaling smokes determine their value for military use. color, visibility, duration, and volume. In addition, the smokes must be nontoxic in ordinary field concentrations.[1]

Signaling smokes are produced by volatilizing and condensing a mixture containing an organic dye. Of the dyes tested, the most satisfactory are azo, anthraquinone, azine, or diphenylmethane compounds. The filling for a colored-smoke munition is essentially a pyrotechnic mixture of fuel and a dye, with a cooling agent sometimes added to prevent excessive decomposition of the dye. The heat produced by the fuel volatilizes the dye which then condenses outside the munition to form the colored smoke. The fuel is made up of a mixture of an oxidizing agent, such as potassium chlorate, and a combustible material, such as sulfur or sugar. The burning time can be regulated by adjusting the proportions of oxidant and combustible material, and by the use of coolants such as sodium bicarbonate.[1]

Each grenade contains a starter mixture and a colored-smoke mixture. Table 1 gives the ingredients, and the percentage of each used in currently standard color mixtures and in the starter mixture for the M18 grenade. The starter mixture is the same for each color. Other colored smoke grenades have approximately the same composition as the M18.[1]

The operational use of signaling smoke can be expected to result in single and repeated inhalation exposures to low, moderate, and high concentrations of the disseminates. In addition, the materials may contaminate soil, foliage, equipment, or vehicles, and may contact the skin, be rubbed into the eyes, or ingested if transferred to rations. In most cases personnel will be exposed only occasionally, but in certain instances, i.e., training exercises, drop-zone and helicopter-operations training, and field testing, personnel may be challenged repeatedly by several routes. It is the purpose of this review to evaluate the hazard of the colored smokes to unprotected personnel exposed acutely or repeatedly.

II. CHEMICAL SMOKE INHALATION TOXICITY STUDIES.

A. Experimental.

In 1966 and 1967 the Toxicology Department, Medical Research Laboratory,* performed acute inhalation studies for the Weapons Development and Engineering Laboratory of red, green, and violet smokes disseminated from M18 munitions.** The work compares the toxicities of the standard smokes with M18 prototype grenades containing sodium picrate pyrotechnic fuels. Yellow smoke was not studied because in preliminary tests it produced an unstable aerosol within the test chamber which resulted in rapid coagulation of the smoke particles and subsequent fallout of the cloud.

The red, green, and violet smokes were tested in the monkey, dog, goat, swine, rabbit, rat, and guinea pig. The particles in these disseminates had an average mass median diameter (MMD) of 1.0 micron over concentration ranges of from 1450 to 17,946 mg/cu m. Except for settling, the smoke clouds remained relatively stable (no particle growth through coagulation) for exposure periods of 10 to 240 minutes.

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* Now Toxicology Division, Biomedical Laboratory.

** Unpublished data. Toxicology Department, Medical Research Laboratory, Edgewood Arsenal, Maryland.

Table 1. Standard Loading for M-18 Colored Smoke Grenades

Smoke	Military specification	Identification of dyes		M18 grenade formulations	
		Chemical nomenclature	Trade name	Component	Weight
					%
Red	MIL-D-3284C 24 June 1971	1-Methylaminoanthraquinone	Disperse Red 9	Dye, Disperse Red 9 Sodium bicarbonate Potassium chlorate Sulfur	40 25 26 9
Yellow	MIL-D-0050029C(MU) 26 April 1968	Dibenzo [b, def] chrysene-7, 14-dione	Dye, Vat Yellow 4	Vat Yellow 4 Benzanthrone Sodium bicarbonate	14 24.5 33.0
	MIL-D-0050074C(MU) 9 May 1968	7H-Benz [de] anthracene-7-one	Dye, benzanthrone	Potassium chlorate Sulfur	20.0 8.5
Green	MIL-D-003277(MU) 26 March 1968	1,4-Di-p-toluidinoanthraquinone	Dye, Solvent Green 3	Solvent Green 3 Vat Yellow 4 Benzanthrone	28 4 8
	MIL-D-0050029(MU) 26 April 1968	Dibenzo [b, def] chrysene-7-14-dione	Dye, Vat Yellow 4	Sodium bicarbonate Potassium chlorate Sulfur	22.6 27 10.4
	MIL-D-0050074C(MU) 9 May 1968	7H-Benz [de] anthracene-7-one	Dye, benzanthrone		
Violet	MIL-D-3691B 20 July 1970 (Violet smoke mix dyes preblended)	1,4-Diamino-2,3-dihydroanthraquinone (80 ± 2%) 1-Methylaminoanthraquinone (20 ± 2%)	Chemical name Disperse Red 9	Violet smoke mix Sodium bicarbonate Potassium chlorate Sulfur	42 24 25 9
Starter mix*				Potassium nitrate Sulfur Sodium bicarbonate Corn starch	43.2 16.8 30.0 10.0

* 60 gm blended with 1.6 gm nitrocellulose binder.

All tests were conducted in a 20,000-liter test chamber that was operated statically during testing. The exposure concentrations were maintained by firing grenades sequentially throughout each exposure period. Depending on the desired Ct,* from 1 to 12 grenades were used.

The rats and guinea pigs were housed in compartmented cages during exposure; the monkeys were caged separately; and the rabbits were penned in groups of six. Dogs, swine, and goats were not caged or restrained.

All animals tested were observed for toxic signs for 30 days postexposure.

B. Analytical.

1. Red Dye Mix.

The compound was analyzed in both the visible and ultraviolet regions. The solvent used in both procedures was absolute ethanol. The visible wavelength was 460 mμ The ultraviolet wavelength was 312 mμ.

A sample of the compound was collected after dissemination from an M18 grenade and analyzed for spectral changes due to thermal decomposition. The spectra (before and after dissemination) showed no shift of peak locations Therefore, the ultraviolet method of analysis was used for the entire program of study.

2. Violet Dye Mix.

The violet dye mixture must be analyzed from the collected product of the grenade dissemination. When the grenade mixture (before firing) is analyzed in either the visible or ultraviolet regions, the following formation was found: the visible region gave two peaks; one at a wavelength of 458 mμ and the other at 486 mμ. The ultraviolet spectra gave a peak at 248 mμ.

When the mixture was fired and disseminated from a grenade, it was found that the compound underwent a chemical change and gave a completely different set of spectra. The visible peaks now appeared at wavelengths of 548 mμ and 588 mμ. The ultraviolet spectra showed peaks at 247 mμ and 304 mμ. With further study of spectral shifts it was found that the major component (1,4-diamino-2,3-dihydroanthroquinone) underwent the largest spectral shift. The visible peaks were again found at 458 mμ and 486 mμ. The ultraviolet spectra gave one intense peak at a wavelength of 250 mμ. With chemical oxidation, the spectral shift could be followed, but not completed. Since the thermal temperature of the grenade gave the oxidation wanted, the collected and dissolved dissemination product was used to give standards for the analytical procedure. An ultraviolet wavelength of 304 mμ was used. Samples were dissolved in absolute ethanol.

3. Green Dye Mix.

The sample was dissolved in absolute ethanol and spectra obtained in both the visible and ultraviolet regions. The visible peak appeared at 396 mμ and the ultraviolet at a wavelength of 247 mμ. Upon dissemination, the green dye gave no spectral shifts. An ultraviolet wavelength of 247 mμ was used.

* Concentration X time of exposure.

C. **Results.**

1. **Lethality.**

A summary of the acute inhalation toxicities of the three smokes in the seven species tested is presented in table 2. The LCt_{50} values shown represent a Bliss analysis of the combined mortality responses of the total number of animals of all species exposed to the individual colors.

Table 2. Acute Inhalation Toxicities of Red, Green, and Violet Smokes Disseminated from M18 Grenade

Smoke	Ranges		LCt50 (combined response of all species)	Slope
	Concentration	Exposure time		
	mg/cu m	minutes	mg min/cu m	
Red	2753-17946	10-240	647, 470 (568, 611-737, 265)*	2.96
Green	3346-13085	18-112	319, 447 (296, 564-344,095)	5.50
Violet	1344- 7830	8-142	211, 205 (182, 107-244,952)	2.20

* Numbers in parentheses are 95% confidence limits.

The times to death of all species tested are shown in table 3.

The details of the inhalation testing in all species exposed to the three colored smokes are shown in tables A-1, A-2, and A-3, appendix A.

2. **Postexposure Observation.**

During exposure, close observations of the animals were not possible due to the density of the smoke clouds. Starting at the time animals were removed from the chamber, observations were recorded in fractions of an hour until the pattern of signs had stabilized, then daily over the next 30 days.

The frequency, onset, and duration of toxic signs seen in the animals exposed to red, green, and violet smoke are described below and tabulated in table 4.

a. **Red Smoke.**

Immediately after exposure, all animals showed signs of upper respiratory tract irritation, much like the effects produced by dust exposures. All species salivated. Gagging was seen in the dog, swine, goat, and monkey as the animals attempted to remove the dusts deposited in the upper respiratory tract. Dogs, goats, monkey, and swine regurgitated a very thick, red mucus and their urine was dark red for 24 hours after exposure. Labored breathing, seen in all species, lasted 7 days. The swine and goat were the most resistant of the seven species tested. Most of the deaths occurred in the first 24 hours (82%, all species cumulated); by 14 days, 97.4% of the deaths had occurred.

Table 3. Times to Death in Seven Animal Species Exposed to Chemical Smokes Disseminated from the M18 Grenade

Day of death	No. of deaths on given day			Cumulative no. of deaths			Cumulative percent of deaths		
postexposure	Red[a]	Green[b]	Violet[c]	Red	Green	Violet	Red	Green	Violet
<1	140	201	160	159	208	148	82.0	90.8	89.7
1	2	6		161	216	148	83.0	94.3	89.7
2	7	3	4	168	219	152	86.6	95.6	92.1
3	2	2		170	221	152	87.6	96.5	92.1
4	8		2	178	221	154	91.8	96.5	93.3
5	2	3		180	224	154	92.8	97.8	93.3
6			1	180	224	155	92.8	97.8	94.0
7	3	1		183	225	155	94.3	98.3	94.0
8	1	1		184	226	155	94.8	98.7	94.0
9	1	1		185	227	155	95.4	99.1	94.0
10	2			187	227	155	96.4	99.1	94.0
11	1			188	227	155	96.9	99.1	94.0
12				188	227	155	96.9	99.1	94.0
13				188	227	155	96.9	99.1	94.0
14	1			189	227	155	97.4	99.1	94.0
15		1	1	189	228	156	97.4	99.6	94.5
16	2	1		191	229	156	98.5	100	94.5
17			2	191	229	158	98.5		95.7
18				191	229	158	98.5		95.7
19				191	229	158	98.5		95.7
20			1	191	229	159	98.5		96.4
21	3		2	194	229	161	100		97.6
22			1	194	229	162			98.2
23			1	194	229	163			98.8
24				194	229	163			98.8
25			1	194	229	164			99.4
26				194	229	164			99.4
27				194	229	164			99.4
28			1	194	229	165			100
29				194	229	165			
30				194	229	165			

a 416 animals exposed.
b 426 animals exposed.
c 485 animals exposed.

Table 4. Signs Observed in Seven Animal Species Following Inhalation Exposure to Red, Green, and Violet Smoke Disseminated From the M18 Grenade

Smoke	Toxic sign	Time to onset						
		Dog	Swine	Goat	Monkey	Rabbit	Rat	Guinea pig
		hours						
Red	Nasal irritation	0.25	2	2	2	1.5	0.25	0.25
	Salivation	0.25	2	2	2	1.5	0.25	0.25
	Gagging	0.25	2	2	2	—	—	—
	Regurgitation	0.25	2	2	2	—	—	—
	Respiratory difficulty	24	24	24	24	24	24	24
	Death	2-336	2-228	1-2.5	2.3-18	1.5-192	1.5-504	0.5-96
Green	Respiratory difficulty	0.5	1	1	1	0.5	0.5	0.5
	Gagging	0.5	1	—	0.5	—	—	0.5
	Vomiting	0.5	1	—	1	—	—	—
	Generalized weakness	0.5	1	1	1	0.5	0.5	0.5
	Dyspnea	1	1	1-1.5	1	1	1	0.5
	Prostration	1	1	1-1.5	0.5	0.5	1	0.5
	Death	<1-408	1-162	1-44	0.5-19	0.5-19	0.5-56	0.5-24
Violet	Respiratory difficulty	1	1	1	1	1	1	0.25
	Gagging	1	—	1	1	1	1	1
	Vomiting	1-24	1	—	—	—	—	—
	Wheezing	1-24	—	1-48	1-48	1-24	1	1
	General weakness	1-48	1	1	1-24	1-24	1	1
	Ataxia	1-24	1	1	—	—	—	—
	Prostration	1-48	0.5-1	1	1-48	1	1	1
	Death	1-96	1-48	1-48	1-672	1-504	0.5-168	1-480

b. Green Smoke.

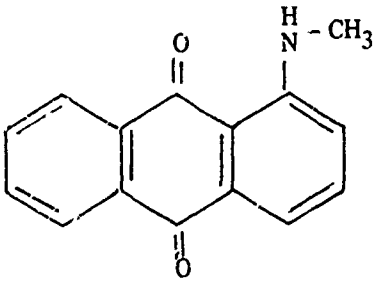
All animals exposed to the green smoke were initially affected by respiratory impairment followed by generalized weakness, dyspnea, and prostration. Prostration lasted as long as 96 hours in the dog; other species generally recovered in 2 to 24 hours. Diaphragmatic breathing lasted for as long as 21 days postexposure in the dog. Colored saliva or urine was not observed in any species. Of the seven species tested, the goat and swine were the most resistant (had the highest LD50's). Most deaths occurred in less than 24 hours, and by 7 days 98.3% (all species cumulated) of the deaths had occurred.

c. Violet Smoke.

In general, the signs caused by exposures to violet smoke mimicked those seen in tests with red and green smokes. All animals showed most of the following signs: respiratory difficulty, gagging, vomiting, wheezing, generalized weakness, ataxia, and prostration. Prostration was noted in all species for 1 to 4 hours; after the animals were able to stand, they remained weak and lethargic for at least 24 hours. Colored saliva or urine was not observed in any species. Most deaths occurred within the first week after exposure.

III. REVIEW OF TOXICITIES OF DYES USED IN CHEMICAL SMOKES.

A. 1-Methylaminoanthraquinone.



This dye comprises 40% of the formulation of the red smoke grenade. In this grenade, 1-methylaminoanthraquinone is the only dye used. In the violet smoke grenade, 80 parts of 1,4-diamino-2,3-dihydroanthraquinone are blended with 20 parts of 1-methylaminoanthraquinone to form the color mixture. This mixture comprises 42% of the violet grenade formulation. The military specification is furnished in appendix B.

1. Toxicology.

a. Local Effects.

This dye causes skin irritation and sensitization, that is, its action on the skin may be delayed by 2 weeks or so and may cause the individual to become more sensitive to it on repeated exposures.*

9 b. Systemic Toxicity.

By the oral and inhalation routes, 1-methylaminoanthraquinone is reported as having slight systemic toxicity when administered acutely, and slight local and systemic toxicity when given chronically.

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* Unpublished data. US Army Environmental Hygiene Agency, Edgewood Arsenal, Maryland.[9]

The US Naval Ordnance Laboratory, as cited by Parent,[2] assigns a toxicity rating of "1." as defined by Sax,[3] to 1-methylaminoanthraquinone when inhaled or swallowed. Rating 1 is defined as a slight toxicity, meaning that any effects are temporary and disappear following termination of exposure with or without medical treatment.

c, Carcinogenicity.

On the basis of its structure, this dye may be a potential liver carcinogen. The carcinogenicity of the anthraquinone part of the molecule has been reported by Japanese investigators, but confirmatory reports have not been forthcoming. The carcinogen most closely related to this compound is 1-aminoanthracene, which would not be formed from this compound in the body.*

In 1968 Griswold *et al.*[4] evaluated the carcinogenicity of 1-methylaminoanthraquinone using as a criterion the exquisite sensitivity of the mammary gland of female rats to certain carcinogens. Ten doses of 500 mg/rat, which was established as the maximally tolerated dose (MTD),[5] were given 3 days apart to nineteen 40-day-old female rats through an intragastric tube. A group of 40 positive controls was given a single dose of 18 mg of DMBA (7,12-dimethylbenz[a]anthracene) as a check on the constancy of responsiveness of the animals. Another group of 140 controls** was given only the sesame oil vehicle.

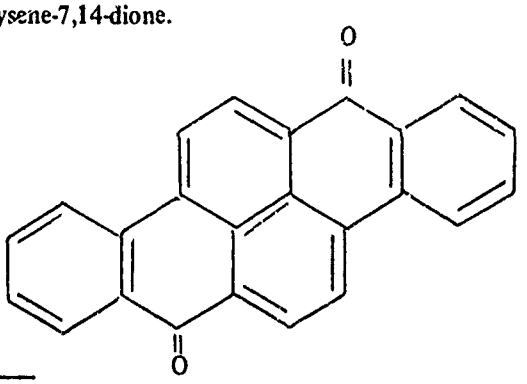
The animals were observed for 9 months to maximize the sensitivity of the test with respect to mammary tumor formation and to discover lesions in other sites.

Eighteen of the rats were autopsied. Grossly apparent lesions were recorded. The pituitary and adrenal glands, kidneys, spleen, and liver were weighed. Any diseased tissues as well as mammary tissue, intestinal tract, pituitary, liver ovaries, and adrenals were fixed in 10% formalin and processed for histologic examination. Representative portions of other viscera were fixed for later examination if indicated.

The results are shown in table 5. One rat died within 45 days, which was shortly after termination of the administration of the compound, and which reflects toxicity resulting from the treatment. The survivors at the end of the experiment reveal the chronic effects, and 14 of the 19 rats survived the 9-month period.

From the data shown in table 5, Griswold *et al.*[4] concluded that 1-methylaminoanthraquinone had little toxicity and no carcinogencity. However, a tubular adenocarcinoma of the kidney was seen in one rat given this compound and was not seen in a group of controls given only the sesame oil vehicle.

B. Dibenzo [b, def] chrysene-7,14-dione.



* Unpublished private communication. Alfred Tatyrek, Picatinny Arsenal, and Dr. Hans Falk, Chief, Carcinogenesis Studies Branch, National Cancer Institute, National Institutes of Health, Bethesda, Maryland.

** Such large groups of controls were used because the authors were also testing 34 other compounds.

Table 5. Evaluation of Carcinogenicity in Female Rat Mammary Glands After Doses of 1-Methylaminoanthraquinone and DMBA

Compound	Total dose	No. of rats remaining			No. autopsied	No. of rats with mammary lesions	Type and no. of mammary lesions	Other lesions
		0 days	45 days	9 mos				
	mg/rat							
1-Methylaminoanthraquinone	5000	19	18	14	18	1	Hyperplasia, 1	Tubular adenocarcinoma of kidney, 1
DMBA (positive control)	18	40	35	19	29	29	Carcinoma, 75; fibroadenoma, 10; hyperplasia, 47	Hyperplasia of lymph nodes, 2; carcinoma of pancreas, 1; lymphocytic infiltration of liver and lymph node, 2; abdominal reticulum cell granuloma, 1
Sesame oil		140	134	127	132	5	Carcinoma, 3; fibroadenoma, 1; hyperplasia, 5	

Various sources refer to dibenzo [b, def] chrysene-7,14-dione as the following:

a. Indantnrene Golden Yellow GK

b. Dibenzo [a, h] pyrene-7,14-dione

c. 3,4,8,9-Dibenzpyrene-5,10-quinone

This dye comprises 14% of the formulation of the yellow smoke grenade, and benzanthrone (7-H-benz[de] anthracene-7-one) comprises 24.5%. The dyes are not preblended before mixing with the other components. The military specification is furnished in appendix C.

1. General Carcinogenetic Considerations.

No tumors were reported by Hartwell[6] in several animal experiments when dibenzo[b,-def] chrysene-7,14-dione was administered by subcutaneous injection and by the percutaneous route. The details of these studies are shown in table 6.

Table 6. Evaluation of Carcinogenicity of Dibenzo [b, def] chrysene-7,14-dione

Animal (no. used)	Route	Dose	Effects	Remarks
Mouse (20)	Subcutaneous	1.2 ml of 0.5% in oil	No tumors	18 alive at 6 months.
Mouse (10)	Subcutaneous	0.5 mg in sunflower seed oil monthly	No tumors	4 died. Experiment lasted 170 days.
Mouse (10)	Percutaneous	0.1% in sunflower seed oil every five days.	No tumors	All died. Experiment lasted 3.5 months.
Mouse (52)	Percutaneous	0.4% in benzene 115 times.	No tumors	30 alive at 6 months. 10 alive at 12 months Experiment lasted 12 months.

Although this compound produced no tumors in the mouse, it is closely related to dibenzochrysene which is a very potent carcinogen.[6-8]* If this latter compound should be present in quantities as small as 0.01% it would represent a considerable hazard.* Doses as small as 10 μg would be considered hazardous.*

Tatyrek[9] in 1965 stated that inasmuch as metabolic changes of quinones to the parent hydrocarbons have never been found, it is unlikely that metabolic reduction of dibenzo[b, def] chrysene-7,14-dione to dibenzpyrene would result.

* Unpublished private communication. Alfred Tatyrek, Picatinny Arsenal and Dr. Han. Falk, Chief, Carcinogenesis Studies Branch, National Cancer Institute, National Institutes of Health, Bethesda, Maryland.[9]

A literature survey from 1965 to the present writing did not reveal any additional information regarding a metabolic reduction of the dione compound to the carcinogenic dibenzochrysene.

Three manufacturers of the Indanthrene Golden Yellow have indicated that there is little possibility of formation of the carcinogenic hydrocarbon in their manufacturing process.* However, recent work (1965) by the Carcinogenesis Studies Branch, National Institutes of Health,** has revealed strong evidence of the presence of a significant quantity (roughly estimated to be of the order of 0.1%) of dibenzochrysene contamination in two different samples of specification grade Indanthrene Golden Yellow dye.

An equally important consideration with the yellow dye is the formation of dibenzpyrene upon burning of a smoke item using compositions containing Indanthrene. Under the conditions of high temperature and a reducing atmosphere such as may be found in a burning smoke item it is possible that some of the quinone groups of the dye may be reduced to the carcinogenic hydrocarbon. This possibility is being investigated and recent studies have disclosed analytical evidence that such a pyrotechnic reduction does take place. Conclusive results cannot be obtained, however, until a pyrotechnic smoke item is made from yellow dye which is entirely free of dibenzpyrene.[9]

2. Local Carcinogenic Effects.

Salimon[10] studied the influence of five carcinogens and four noncarcinogens on the inflammatory process in ear tissue. The carcinogens were: 9,10-dimethyl-1,2-benzanthracene (DMBA), 1,2,5,6-dibenzanthracene,† 3,4-benzpyrene,†† 3,4,8,9-dibenzpyrene (dibenzo[b, def]chrysene), and 20-methylcholanthrene.§ The four noncarcinogens were: anthracene, phenanthrene, pyrene, and 3,4,8,9-dibenzpyrene-5,10-quinone (dibenzo[b, def]chrysene-7,14-dione).

A single application of a 1.5% solution of DMBA in oil upon the ear of rabbits did not cause inflammatory changes visible to the naked eye, but caused marked changes in the capacity of that tissue to react to phlogogenic agents. In the first 3 days the inflammatory reactivity increased and after the 4th and 5th days it decreased.

The hyporeactivity which developed was not accompanied by appreciable morphological changes and persisted for a prolonged period (up to 8 months).

The decrease in the inflammatory reactivity of the ear of rabbits became apparent even after treatment with 0.02% and 0.12% DMBA solutions, i.e., after application of only 25 and 15 μg of that substance, respectively.

The hyporeactivity arose in similar experiments[10] with the other four carcinogens in benzene (0.3%) or oil (M/1000).

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* Unpublished private communications among Alfred Tatyrek, Picatinny Arsenal and personnel of Atlantic Chemical Corporation, General Aniline and Film Corporation, and National Aniline Division of Allied Chemical and Dye Corporation.[9]

** Unpublished private communication. Alfred Tatyrek, Picatinny Arsenal, and Dr. Hans Falk, Chief, Carcinogenesis Studies Branch, National Cancer Institute, National Institutes of Health, Bethesda, Maryland.[9]

† C. A. Subject Index name, dibenz[a, h]anthracene.

†† Benzo(a)pyrene is C. A. Subject Index name.

§ 3-Methylcholanthrene is C. A. Subject Index name.

Among noncarcinogenic hydrocarbons, solutions of pyrene in benzene (0.3%) were found to exert a similar effect, whereas the following solutions had no effect: anthracene (0.3%, 0.5%), phenanthrene (0.3%) and a saturated solution of dibenzpyrenequinone in oil.

A single application of a 50% solution of turpentine in oil under similar conditions did not produce a persistent decrease of the inflammatory reactivity.

A 1.5% solution of DMBA in oil applied 10 to 20 minutes or 3 to 5 hours after the application of the inflammatory agent has no appreciable antiphlogistic action.

Salimon[10] concludes:

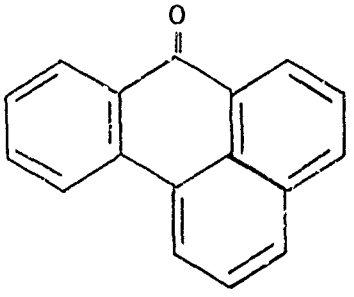
"The data discussed above show that carcinogenic hydrocarbons produce essential functional changes in the state of tissues. The most important of these changes is, in our opinion, the prolonged decrease of the inflammatory reactivity. Such an effect could be found under the influence of all five carcinogenic substances investigated by us; other hydrocarbons (anthracene, phenanthrene and 5,10-quinone of 3,4,8,9-dibenzpyrene), which do not produce tumors, were inactive in the above aspect.

"The results of the experiment with pyrene warrant the conclusion that a substance which sometimes causes papillomas and decreases the inflammatory reactivity can be classified as a 'subcarcinogen' agent, in other words, represents a substance which occupies an intermediate position between absolute carcinogenic and noncarcinogenic hydrocarbons.

"Finally, we have to emphasize one more aspect regarding the above investigation: it cannot be excluded that the decrease of the inflammatory reactivity taking place under the influence of carcinogenic substances was, in actual fact, even more intensive than it appeared in our experiments. The method used by us enabled us to assess only relative changes in the reactivity of the tissue in the area treated with the carcinogenic substance, as compared with a symmetrical (control) area of the body. We gained, however, the impression that carcinogenic substances cause not only a marked local but also, to a certain degree, a general decrease of the inflammatory reactivity all over the body This fact could be observed in experiments in which the inflammation was produced after a relatively long period had elapsed since the carcinogenic substance had been applied and had been manifest in the fact that the inflammatory process acquired the tendency to take a somewhat langued course.

"If this preliminary conclusion is correct, the data presented above require a certain correction in the sense that the decrease of the inflammatory reactivity under the influence of carcinogenic hydrocarbons is of more intensive and prolonged character than it appears from our experiments."[10]

C. 7H-Benz[de]anthracene-7-one.



Benzanthrone (7H-benz[de]anthracene-7-one) comprises 24.5% of the formulation of the yellow smoke grenade and dibenzo[b,def] chrysene 7,14-dione comprises 14%. The military specification is furnished in appendix D.

1. Local Effects.

Benzanthrone was nonirritating when applied to both clipped intact and abraded skin of guinea pigs and allowed to remain 24 to 48 hours.[11]*

Dermatitis has resulted in man from occasional contact with benzanthrone. It is said to exert a photodynamic effect which results in the production of an actinic dermatitis and melanosis or leukoderma [12] Lanza and Goldberg[13] list benzanthrone as a cause of dermatitis in man, but only in hypersensitive individuals.

The incidence of hyperpigmentation (melanosis) in 25 employees of a dye factory is reported by Uebelin and Buess. Their study also described the skin irritancy of benzanthrone postulating that the cutaneous irritation is probably due to two substances which form at the time of the anthraquinone reduction in the dye production process. anthracene, which is undoubtedly still present in trace amount, and some nonsaturated fatty acids (like acrylic acid) probably resulting from a transformation of glycerine. Of more interest to the authors, however, is the effect described as thinning of the epidermis, flattening of papillary corpuscles, the edema caused by laxity of the papillary layer and subpapillary layer, and the infiltration of round cells into this stratum. In the superficial layer of the cells, just to the boundary between the upper third and middle third, there is a row of chromatophores arranged in bands which encloses the melanin. These integumentary changes do not appear to affect the general health of the workers except that minor changes in liver function were noted. The degree of pigmentation was seen to vary considerably over the affected body areas with greatest intensities being noted around the eyes, at the neck and nape of the neck, the upper thorax, and sometimes also on the hands and forearms. The skin coloration takes on all shades from orange to blue-black, passing through brown. It is particularly intense in summer, in high temperatures, and after exposure to the sun. Various theories are presented to explain the creation of the pigment including the degradation of adrenalin, hormonal inbalances that are believed to be of hypophysical origin, and the existence of noxious factors absorbed by way of respiration.[14]

Further evidence of skin discolorations in benzanthrone workers was reported by Trivedi and Niyogi. Medical examinations were performed on 48 workers employed in a benzanthrone plant where some individuals were reported as having a blackening of the skin. Thirty percent of those examined had blackening of the skin with or without other signs and symptoms, and 14 percent had only a burning sensation, nausea, cough, etc No abnormalities were detected in blood or urine. The range of the incubation period for blackening of skin was 1 to 35 months and the average was 8-1/2 months. Keratosis was noted in two workers.[15]

2. Systemic Toxicity.

Benzanthrone intoxication in humans affects the functional state of the liver and is manifested by disturbances of the autonomic nervous system. The functional state of the liver may be used for diagnostic purposes, especially in cases of residual effects.[16] Apparently patients suffering from benzanthrone intoxication will exhibit an increase of hippuric acid and its excretion, and an increase in the total content of protein in blood and serum albumins if given a therapeutic dose of carbocholine, $H_2NC(.O)OCH_2\text{-}CH_2N(CH_3)_3.Cl$, which explains the disturbance of regulatory functions of the autonomic nervous system. [17]

* Unpublished data. Jacobson, K. M. Monthly Technical Progress Report on Chemical Corps Research Development Projects. Project 4-61-14-002, US Air Force. Health Hazards of Military Chemicals. 31 October 1959.

The effect of benzanthrone on the blood, adrenal, and liver ascorbic acid levels in adult male guinea pigs was investigated by Pandya, Singh, and Joshi.[18] Benzanthrone and ascorbic acid were administered intraperitoneally and orally in doses of 25 mg and 50 mg/kg body weight respectively. Benzanthrone alone caused a significant decrease in ascorbic acid levels in the blood, adrenals, and liver. Supplementation of ascorbic acid appreciably restored the blood ascorbic acid However, adrenal and liver ascorbic acid levels were restored only to some extent. Histochemical examination of ascorbic acid in the adrenals revealed almost similar changes. The mortality rate due to benzanthrone toxicity (500 mg/kg) was lowered by 40% in nonscorbutic as compared to scorbutic guinea pigs.

Benzanthrone was tested by Epstein *et al.*[19] to determine its mutagenic effects by the dominant lethal assay in the mouse. In this series, a total of 174 test agents, including pharmaceuticals, food additives, pesticides, and organic extracts of air and water pollutants, were tested. Less than 10% of all materials tested were unequivocally mutagenic as determined directly by increased early fetal deaths per pregnancy. Additionally, about 5% of all materials tested yielded data which fell beyond control limits but which, however, require further replication because of internal inconsistencies The early fetal deaths and preimplantation losses produced by benzanthrone were within control limits, categorizing this compound with the 85% that failed to produce either unequivocal mutagenic effects or other indications of reproductive impairment. The authors point out, however, that while the induction of dominant lethal mutations is indicative of potential genetic hazards to man, inactive agents cannot be regarded as nonmutagenic until additionally tested by *in vivo* cytogenetics and in the host-mediated assay.

Slutskif[17] reported that benzanthrone could be detected in the blood of only 6 of 42 individuals poisoned with the dye. This shows that benzanthrone undergoes changes in the blood (or before entering the blood). The chemical abstract of Slutskif's work did not state routes of administration or subjective symptoms.

Thirty white rats were given water saturated with benzanthrone (up to 400 mg/l) for 4 months.[20] The dose corresponded to a daily dose of 20 mg/kg of body weight for man. The weight of the animals did not change when compared with the weight of a control group. There was no shift in the level of cholinesterase activity or change in the cephalin-cholesterol flocculation tests. Based on these studies, the permissible concentration of benzanthrone in reservoir water was formulated. There data are shown in table 7.

Table 7. Permissible Concentration of Benzanthrone in Reservoir Water

Concentration	Effects
mg/l	
0.05	Imparts noticeable yellow color to water.
5.0 or lower	Daphnia activity not disturbed.
20-50	Taste becomes noticeable
50	Odor becomes noticeable.
50-100	Inhibits the biological oxygen demand but the inhibition does not exceed 18% and has no effect on the practical sanitary preservation of reservoir water. There is no noticeable effect on the ammonification and ultrafiltration processes, nor on the growth and death of the saprophytic microflora of the water.

3. Carcinogenicity.

At present there appear to be conflicting opinions as to whether this material is carcinogenic.[6]*

The tests for carcinogenic action, performed by Morozenskaya,[21] cited by Hartwell,[6] and shown in table 8, reveal that benzanthrone is not carcinogenic in mice given dermal or subcutaneous doses. An evaluation of the same data by Sawicki[22] classed 7H-benz[de] anthracene-7-one (benzanthrone) as having carcinogenic activity, but he also stated that the carcinogenicity of this type of compound needs confirmation and more thorough investigation.

Table 8. Evaluation of Carcinogenicity of Benzanthrone

Route	Dose	Effects	Remarks
Dermal	70-75 mg total dose; 0.5% benzene soln used, 140 applications.	13/50 mice alive at end of 6 months, two of 50 animals developed tumors (one lung, one thyroid).	Morozenskaya believes tumors were not due to benzanthrone but arose spontaneously. Compound not blastomogenic.
Subcutaneous	10 mg total dose; 0.5 soln in olive oil; 5 injections of 0.4 ml, 10-15 days apart.	16/32 alive at 6 months. Two of 32 animals developed tumors (one lung, one jaw).	Conclusion same as above.

Studies by Epstein, *et al.*[23] of 107 polycyclic compounds of "*known* carcinogenicity" (list included benzanthrone**) indicate that there is little relationship between carcinogenicity and charge-transfer complex formation as measured by certain chemical tests. A positive relation did exist between carcinogenicity and photodynamic action as measured with paramecia. Benzanthrone, however, is listed as a + carcinogen within a range from noncarcinogens to +++ carcinogens. Examples of each category are shown in table 9.

Table 9. Examples of Noncarcinogens and Potencies of Carcinogens

Type	Examples
Noncarcinogens	Anthracene, phenanthrene, carbazole
Carcinogens	
Low potency (+)	2-Aminoanthracene, benzanthrone, chrysene
Moderate potency (++)	Dibenz [a, h] anthracene, benzo [c] fluoranthene, 1,2,3,4-dibenzpyrene
High potency (+++)	7-Methylbenz [a] anthracene, benzo [a] pyrene, 3-methylcholanthrene

* Unpublished private communication. Alfred Tatyrek, Picatinny Arsenal, and Dr. Hans Falk, Chief, Carcinogenesis Studies Branch, National Cancer Institute, National Institutues of Health, Bethesda, Maryland.[9]

** Article does not document the "known carcinogenicity" for benzanthrone.

4. **Hygienic Standard.**

New sanitary standards for projected industrial plants were proposed by the KHARIKOV Institute of Labor Hygiene and Occupational Diseases of Academy of Medical Sciences of the U.S.S.R. and the Department of Labor Hygiene of the Central Institute of Post-Graduate Medicine in 1957.

Their proposed maximal allowable concentration for benzanthrone in the air of work rooms and work shops of industrial manufacturing and production plants is 0.002 mg/liter.[24]

5. **Proposed Military Specification.**

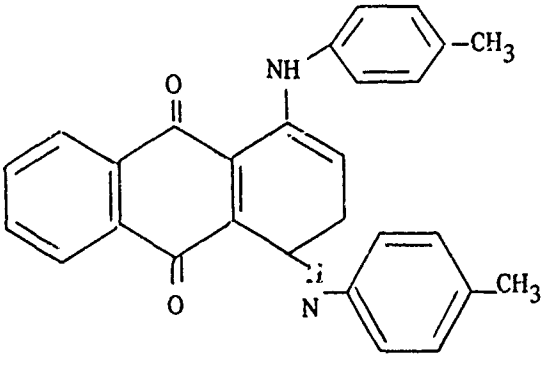
A proposed military specification, MIL-D-50074D, for Dye Benzanthrone (Project Number 6820-0049) was prepared on 16 November 1970. Paragraph 5.2 (Marking) states that: "Marking shall be in accordance with MIL-STD-129. In addition, each container shall be durably and legibly marked with contrasting letters and background to show the net weight of contents and the following information:

CAUTION

CAUSES SEVERE IRRITATION TO SOME PEOPLE. AVOID CONTACT WITH SKIN OR CLOTHING. IN CASE OF CONTACT, FLUSH WITH WATER. WASH CONTAMINATED CLOTHING BEFORE RE-USE. INDIVIDUALS SENSITIVE TO THIS PRODUCT SHOULD NOT CONTINUE TO WORK WITH IT.[25]

The results of a review of the proposed specification by DA, USAEHA, Edgewood Arsenal, Maryland was furnished the Commanding Officer, Edgewood Arsenal, through the Surgeon General on 18 January 1971 It was recommended that a statement restricting the use of benzanthrone to combat situations be included in the proposed specification since the material is a potential carcinogen. Consequently, the proponent of subject specification is advised to substitute for benzanthrone a dye that is potentially less hazardous.[26]

D. **1,4-di-p-toluidinoanthraquinone.**



This dye comprises 28% of the formulation of the green smoke grenade. Two other dyes, Vat Yellow 4 (4%) and benzanthrone (8%), are also present in the mix. The dyes are not preblended. The military specification is furnished in appendix E.

1. Certification for Use (FDA)[27]

a. Drugs and Cosmetics.

D and C Green No. 6 may be certified for use in drugs and cosmetics, provided the following specifications are met:

Volatile matter (at 135°C), not more than 2.0%.

Sulfated ash, not more than 1.0%.

Water-soluble matter, not more than 0.3%.

Matter, insoluble in carbon tetrachloride, not more than 1.5%.

Intermediates, not more than 0.5%.

Pure dye (as determined by titration with titanium trichloride), not less than 96.0%.

Melting point, not less than 210°C.

b. Polyethylene Terephthalate Surgical Sutures.

D and C Green No. 6 shall conform to the following specifications and shall be free from impurities other than those named to the extent that such other impurities may be avoided by good manufacturing practice.

Volatile matter (at 135°C), not more than 2.0%.

Water-soluble matter, not more than 0.3%.

Matter insoluble in carbon tetrachloride, not more than 1.5%.

Intermediates, not more than 0.5%.

Lead (as Pb), not more than 10 parts per million.

Arsenic (as As), not more than 1 part per million.

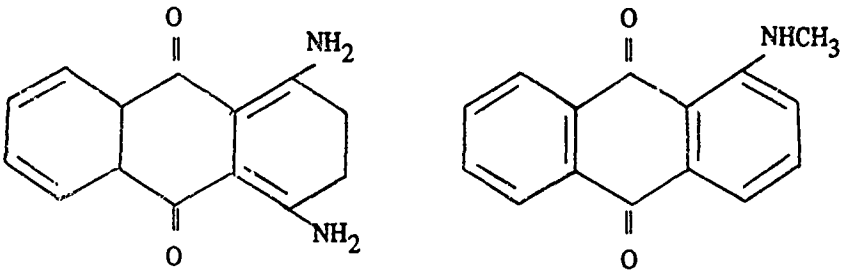
Pure color, not less than 96.0%.

D and C Green No. 6 may be safely used for coloring polyethylene terephthalate surgical sutures.

2. Toxicity, Sensitization Properties, and Carcinogenicity.

A survey of all pertinent literature failed to reveal any information relating to the toxicity, sensitization, or carcinogenic properties of this dye. When mixed with Vat Yellow 4 and benzanthrone in the Green smoke formulations, the effects of the mixture are unknown but the same reaction would probably be evident that results from contact or inhalation of the yellow dyes alone.

E. Dye Mix, Violet.



The violet dye mix comprises 42% of the formulation of the violet smoke grenade. No other dyes are present in this formulation. The military specification is furnished in appendix F.

No biological data were found for the mixture. No data subsequent to 1965 were found on the diamine compound; Tatyrek[9] states that the compound has not been tested but is expected to be relatively safe because of structure. A review of the biological data pertinent to the violet dye mix is shown in table A-3 of appendix I.

IV. DISCUSSION.

A. Acute Inhalation Toxicity of Chemical Smokes Disseminated from the M18 Grenade.

The results of acute inhalation testing of the red, yellow, and violet smokes indicate that these disseminates from M18 grenades are of a low order of toxicity. The extremely high Ct's required to produce deaths and the toxic signs exhibited by the animals after exposure are similar to the responses caused by exposures to nontoxic dusts. Deaths were probably due to suffocation caused by loading of the respiratory tree with smoke particles and the inability of the animal to clear its lungs. A comparison of the toxicities of the smokes with that of CS (0-chlorobenzylidene malononitrile), a commonly used riot control agent, is shown in table 10

Table 10. Acute Inhalation Toxicities of Chemical Smokes and CS

Material	All species LCt_{50} value	LD_{50} ratio Smoke/CS
	mg min/cu m	
Red smoke	647,000	10.6
Green smoke	320,000	5.2
Violet smoke	211,000	3.5
CS[28]	61,000	

B. Toxicity, Sensitization Properties, and Carcinogenicity of Chemical Smoke Dyes.

1. 1-Methylaminoanthraquinone.

This dye causes skin irritation and sensitization which may be delayed 2 weeks or more and may cause the individual to become more sensitive to it on repeated exposures. It has only slight acute and chronic toxicity, however, when administered orally or inhaled.

On the basis of structure this dye may be a potential carcinogen. The carcinogenicity of the anthraquinone part of the molecule has been reported by Japanese investigators but has not been confirmed.

In an evaluation conducted by Griswold[4] in 1968 the dye was shown to have little toxicity and no carcinogenicity in the breast but single lesions were seen at other sites. This did not occur in controls.

It may be concluded from these studies that 1-methylaminoanthraquinone could be considered to be a skin irritant and sensitizer with possible carcinogenic activity.

2. Dibenzo[b, def] chrysene-7-14-dione.

This dye was judged to be noncarcinogenic by Salimon[10] in comparative studies with carcinogenic and noncarcinogenic hydrocarbons where the inflammatory process in rabbit ear tissues was used to determine the classification of the test substances.

In subcutaneous and percutaneous studies reported by Hartwell[6] the compound produced no tumors in the mouse But it was pointed out that the compound is closely related to dibenzochrysene, a potent carcinogen. If this latter compound should be present in quantities as small as 0.01%, it would represent a considerable hazard. Doses as small as 10 μg are considered hazardous. There is a distinct possibility that this degree of contamination may be present as shown in recent studies of the National Institutes of Health, where 0.1% of dibenzochrysene contamination was found in two different samples of specification grade Indanthrene Yellow Dye 3.

An equally important consideration is the formation of dibenzpyrene from burning of a smoke item using compositions containing Indanthrene. It is distinctly possible that some of the quinone groups of the dye may be reduced to carcinogenic hydrocarbons. Recent studies have disclosed analytical evidence that such a pyrotechnic reduction does take place.

This dye as commercially produced may be considered to be a potential carcinogen due to contaminants not defined by specifications and, of more importance, may break down during thermal dispersion to carcinogenic materials.

3. 7 H-Benz [de] anthracene-7-one.

Dermatitis has resulted in man from occasional contact with benzanthrone, exerting a photodynamic effect which results in the production of actinic dermatitis, melanosis, or leukoderma.

Benzanthrone intoxication in humans affects the functional state of the liver and is manifested by disturbances of the autonomic nervous system .

There are conflicting opinions as to whether benzanthrone is carcinogenic. Hartwell[6] and Morozenskaya[21] report negative results in mice tested dermally and subcutaneously while Epstein[23] lists benzanthrone as a known carcinogen of (+) potency. This designation places the compound in the least carcinogenic category but would seriously restrict usage, and would strengthen the argument to replace benzanthrone with a dye potentially less hazardous.[25,26]

At the very best, or until evidence is made available which would refute the rating assigned the compound by Epstein, benzanthrone should be considered a weak carcinogen.

4. 1,4-di-p-toluidinoanthraquinone.

This dye has been certified for use in drugs and cosmetics, as well as for coloring polyethylene terephthalate surgical sutures. There is no information available, however, on the toxicity, sensitization properties, and carcinogenicity of this dye nor on any other biological effects.

5. Dye Mix, Violet.

There are no biological data available relating to mixtures of 1,4-diamino-2,3-dihydroanthraquinone and 1-methylaminoanthraquinone. Based on structure alone, however, the diamino compound may be considered to be relatively safe. The inhalation toxicity of the violet dye mix is shown in table A-3. Since 20% of the violet dye mix is 1-methylaminoanthraquinone, skin contact would most probably cause similar effects to those caused by the pure compound (skin irritation and sensitization). The same carcinogenic hazard would be present in handling the mix as for unmixed 1-methylaminoanthraquinone.

V. CONCLUSIONS.

From a review of the available data relating to the disseminated smokes and the dyes used in chemical smoke formulations it is apparent that many knowledge gaps exist. To adequately characterize the dyes and to define the hazards incident to their use in manufacturing processes and in military operations, the following studies should be performed.

1. Subacute and chronic inhalation studies with red, green, violet, and yellow smokes (provided stable aerosol clouds can be maintained).

2. Acute and chronic skin and eye studies and dermal sensitization with the disseminated smoke products.

3. Cancer studies with either the smokes or with the disseminated smoke products.

4. Reproductive (mutagenic, teratogenic, etc.) studies with either inhalation of the smokes or parenteral injection of the disseminated smoke products.

5. Definitive chemical studies to characterize the specification dyes as well as the disseminates from the M18 grenade.

All studies should be performed with the following materials:

a. Dye, Disperse Red

b. Dye, Vat Yellow 4

c. Dye, Benzanthrone

d. 36/64% mixture of b and c

e. Dye, Solvent Green 3

f. 70/10/20% mixture of b, c, and e

g. 1,4-diamino-2,3-dihydroanthraquinone

h. 80/20% mixture of a and g

In addition to the above work, concurrent research should be initiated to find substitutes for Disperse Red, Vat Yellow 4, and benzanthrone. Selected candidates could then be tested to determine their relative potencies and possible hazards to unprotected individuals

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26. USAEHA-MT (10 December 1970), 2nd Ind, Subject: Proposed Military Specification MIL-D-50074D, Dye Benzanthrone (Project Number 6820-0049), Thru: The Surgeon General, Attn: MERDD-SC, Department of the Army, Washington, D.C. 20315, To: Commanding Officer, Edgewood Arsenal, Attn: SMUEA-QAES, Edgewood Arsenal, Maryland 21010.

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Table A-1. Inhalation Toxicity of Red Smoke Dispersed from an M18 Munition in Seven Animal Species (30-Day Observation) With a Bliss Statistical Analysis

Species	Ct	Concentration	Exposure time	Mortality fraction	Times to death	Statistical analysis				
						Mortality	LD	Lower limit	Upper limit	Log X
	mg min/cu m	mg/cu m	min		hr	%				
Monkey	1,029,425	7,625	135	6/6	2(5),* 18(1)	1	789,623	765,348	814,666	16.9
	814,940	3,396	240	3/6	4(3)	16	804,060	793,139	815,131	
	788,158	5,254	150	0/6	–	30	809,219	795,093	823,930	
	726,850	4,846	150	0/6	–	50	815,013	801,713	828,534	
	648,640	4,324	150	0/6	–	84	826,115	811,565	840,926	
	331,000	2,758	120	0/6	–	99	841,219	803,096	881,152	
Dog	1,112,795	8,243	135	6/6	–	1	164,148	82,367	327,126	5.2
	726,850	4,846	150	4/6	2(3), 48(1)	16	294,553	204,456	424,351	
	648,640	4,324	150	5/6	2.5(1), 18(3), 96(1)	30	362,072	274,179	478,140	
	453,980	3,775	120	5/5	24(1), 48(3), 336(1)	50	455,805	360,693	575,999	
	331,000	2,758	120	2/6	48(1), 168(1)	84	705,335	493,470	1,008,163	
	255,084	9,110	28	0/6	–	99	1,265,680	641,316	2,497,899	
	179,460	17,946	10	0/6	–					
Goat	1,112,940	8,243	135	3/6	1(1), 2(1), 5(1)					
	814,940	3,396	240	0/6	–					
	648,640	4,324	150	0/6	–		No probit feasible			
	331,000	2,758	120	0/6	–					
Swine	1,112,795	8,243	135	2/6	2(1), 228(1)					
	814,940	3,396	240	1/6	4(1)					
	751,890	5,013	150	0/6	–		No probit feasible			
	331,000	2,758	120	0/6	–					
Rabbit	814,940	3,396	240	6/6	4(3), 48(1), 120(2)	1	371,969	228,584	605,294	11.5
	788,158	5,254	150	5/6	2.5(2), 17(1), 72(2)	16	485,489	367,224	641,842	
	751,890	5,013	150	5/6	96(3), 168(1), 192(1)	30	533,347	430,817	660,277	
	588,615	6,925	85	4/6	18,(1), 96(2), 168(1)	50	592,306	507,108	691,852	
	433,560	3,613	120	0/6	–	84	722,660	615,254	848,816	
						99	943,207	671,632	1,324,594	
Rat	1,029,425	7,625	135	20/20	2(20)	1	298,669	153,657	580,535	7.93
	788,158	5,254	150	19/20	2.5(13), 18(1)	16	439,704	134,072	615,591	
	751,890	5,013	150	9/20	2(3), 18(6)	30	504,023	402,489	631,171	
	588,615	6,925	85	17/20	1.5(17)	50	586,934	522,338	659,519	
	433,560	3,613	120	1/20	2(1)	84	783,462	643,842	953,358	
	255,084	9,110	28	0/20	–	99	1,153,422	687,998	1,933,699	

Table A-1. (Contd)

Species	Ct	Concentration	Exposure time	Mortality fraction	Times to death	Statistical analysis				
						Mortality	LD	Lower limit	Upper limit	Log X
	mg min/cu m	mg/cu m	min		hr	%				
Guinea pig	1,029,425	7,625	135	20/20	2(20)	1	100,587	42,506	238,032	4.27
	751,890	5,013	150	18/20	2(18)	16	206,277	138,333	307,593	
	588,615	6,925	85	19/20	1.5(1)	30	265,796	206,967	341,347	
	433,560	3,613	120	10/20	18(5), 24(1), 48(2) 96(2)	50	352,667	304,976	407,815	
	255,084	9,110	28	1/20	0.5(1)	84	602,946	417,026	871,753	
	194,200	6,473	30	9/20	18(1), 349(2), 264(1) 334(2), 504(3)	99	1,236,484	539,950	2,831,547	
	179,460	17,946	10	0/20	–					
All rodents	–	–	–	–	–	1	129,011	48,844	340,754	4.06
						16	274,362	177,347	424,448	
						30	358,091	277,700	461,755	
						50	481,976	434,868	534,188	
						84	846,696	569,155	1,259,581	
						99	1,800,632	709.635	4,568,933	
Non rodents	–	–	–	–	–	1	19,004	94,004	389,506	3.45
						16	465,323	365,110	593,092	
						30	636,800	550,140	737,110	
						50	903,586	716,878	1,138,922	
						84	1,754,551	988,875	3,113,080	
						99	4,266,873	1,469,244	12,391,549	
All species	–	–	–	–	–	1	105,392	35,769	130,533	2.96
						16	297,969	194,215	457,148	
						30	430,024	348,686	530,337	
						50	647,470	568,611	737,265	
						84	1,406,916	787,396	2,513,873	
						99	3,977,709	1,155,920	13,687,943	

* Figures in parentheses are numbers of animals dying.

Table A-2. Inhalation Toxicity of Green Smoke Disseminated from the M18 Munition in Monkeys, Dogs, Swine, Goats, Rabbits, Rats, and Guinea Pigs With a Statistical Analysis of These Data

Species	Ct	Concentration	Exposure time	Mortality fraction	Times to death	Bliss Statistical Analysis				
						Mortality	LD	Lower limit	Upper limit	Slope (log X)
	mg min/cu m	mg/cu m	min		hr	%				
Monkey	512,680	8,269	62	6/6	1(6)*	1	146,779	27,074	795,752	12.6
	357,409	11,914	30	1/6	1(1)	16	187,290	90,020	399,665	
	293,035	7,711	36	6/6	0.75(5), 19(1)	30	402,117	138,756	300,269	
	224,254	4,771	47	1/6	<1(1)	50	224,678	196,475	256,930	
	201,476	4,797	42	2/6	<1(2)	84	269,528	139,414	521,077	
	83,661	3,246	25	0/6	–	99	343,920	68,199	1,734,605	
Dog	625,975	6,804	92	6/6	1.5(6)	1	73,123	8,841	604,826	4.7
	512,680	8,269	62	5/6	1(1), 2(2), 48(2)	16	141,143	47,888	415,995	
	293,035	7,711	38	6/6	0.75(1), 19(3), 43(1)	30	178,021	85,745	369,601	
					72(1)	50	230,637	156,355	340,208	
	224,254	4,771	47	2/6	4(1), 336(1)	84	376,875	205,437	691,380	
	201,478	4,797	42	2/6	216(1), 408(1)	99	727,445	145,405	3,639,338	
	78,159	4,342	18	0/6	–					
Swine	622,780	9,885	63	6/6	1(6)	1	204,045	43,385	955,254	6.7
	595,482	9,605	62	6/6	1(5), 172(1)	16	322,111	154,265	672,579	
	492,220	7,939	62	2/6	1(2)	30	378,438	238,188	601,269	
	457,973	13,085	35	1/6	0.5(1)	50	452,968	364,554	562,824	
	403,972	6,516	62	0/6	–	84	636,984	366,863	1,105,994	
	224,254	4,771	47	1/6	168(1)	99	260,243	260,243	3,885,406	
	201,478	4,797	42	0/6	–					
Goat	1,330,090	11,876	112	3/6	<2(3)	1	160,599	10,507	2,454,841	3,67
	625,975	6,864	92	5/6	1.5(4), 44(1)	16	436,213	199,359	954,469	
	512,680	8,269	62	1/6	1(1)	30	620,693	407,486	945,458	
	492,220	7,939	62	0/6	–	50	919,917	355,301	2,381,772	
	224,254	4,771	47	0/6	–	84	1,939,981	174,439	21,574,980	
	201,478	4,797	42	0/6	–	99	5,269,302	83,136	439,774,850	
Rabbit	595,482	9,605	62	1/6	1(1)	1	301,659	282,807	321,766	44.5
	457,973	13,085	35	5/6	0.5(5)	16	323,170	301,412	346,519	
	409,117	10,766	38	6/6	0.5(6)	30	331,137	306,986	357,188	
	403,972	6,516	62	6/6	1(2), 2(4)	50	340,245	316,389	365,900	
	332,780	11,885	28	2/6	<1(2)	84	358,212	352,012	364,522	
	210,478	6,568	32	0/6	–	99	383,767	339,774	433,457	

Table A-2. (Contd)

Species	Ct	Concentration	Exposure time	Mortality fraction	Times to death	Bliss Statistical Analysis				
						Mortality	LD	Lower limit	Upper limit	Slope (log X)
	mg min/cu m	mg/cu m	min		hr	%				
Rat	595,482	9,605	62	20/20	1(20)	1	176,235	133,654	232,381	10.2
	409,117	10,766	38	19/20	0.5(17),24(1),56(1)	16	238,043	201,410	281,338	
	403,972	6,516	62	18/20	1(18)	30	264,692	231,769	302,293	
	332,780	11,885	28	13/20	<1(13)	50	297,955	269,070	329,942	
	210,160	6,568	32	1/20	23(1)	84	372,948	339,387	409,826	
	83,661	3,346	25	0/20	–	99	503,746	421,273	602,364	
Guinea pig	595,482	9,605	62	20/20	1(20)	1	198,777	150,989	261,689	10.9
	409,117	10,766	38	18/20	0.5(15), 24(3)	16	263,129	224,566	308,213	
	403,972	6,516	62	18/20	1(18)	30	290,511	257,265	328,053	
	332,780	11,885	29	3/20	<1(6), 24(2)	50	324,431	296,940	354,467	
	210,160	6,568	32	1/20	4(1)	84	400,015	355,712	437,537	
	83,661	3,346	25	0/20	–	99	529,517	438,386	639,592	
All rodents	–	–	–	–	–	1	190,737	159,703	227,802	
						16	253,393	228,036	281,569	
						30	280,115	257,824	304,333	
						50	313,263	294,127	333,644	
						84	387,279	364,252	411,761	
						99	514,495	456,467	579,900	
All non rodents (goat not included)	–	–	–	–	–	1	86,705	38,201	196,795	4.2
						16	181,419	122,275	269,172	
						30	235,430	182,605	303,536	
						50	314,856	274,294	361,417	
						84	546,441	401,435	743,825	
						99	1,143,350	552,030	2,368,081	
All species combined (goat not included)	–	–	–	–	–	1	120,503	77,492	187,386	5.5
						16	210,569	169,264	261,952	
						30	256,422	222,194	295,922	
						50	319,447	296,564	344,095	
						84	484.623	418,758	550,853	
						99	846,839	587,799	1,220,036	

* Figures in parentheses are numbers of animals dying.

Table A-3. Inhalation Toxicity of Violet Smoke Disseminated from the M18 Munition in Seven Animal Species

Species	Ct	Concentration	Exposure time	Mortality fraction	Times to death	Bliss Statistical Analysis				
						Mortality	LD	Lower limit	Upper limit	Slope
	mg min/cu m	mg/cu m	min		hr	%				
Monkey	437,900	7,063	62	6/6	1(5),* 19(1)	1	1,817	81	40,711	1.74
	349,440	5,636	62	5/6	18(3), 96(1), 504(1)	16	10,626	2,063	54,733	
	127,240	3,030	42	5/6	140(1), 360(1), 408(3)	30	19,821	6,154	63,835	
	63,166	1,344	47	5/6	20(2), 44(1), 456(1), 576(1)	50	39,731	18,290	86,307	
	21,112	2,111	10	3/6	552(2), 672(1)	84	148,356	49,876	442,471	
	19,500	2,438	8	0/6	–	99	868,765	72,478	10,413,476	
Dog	656,882	10,595	62	6/6	1(6)	1	345,647	322,974	369,911	43.30
	353,012	5,694	62	6/6	1-1/4(1), 3(2), 23(2), 96(1)	16	348,104	336,456	360,155	
	349,400	5,635	62	2/6	18(1), 96(1)	30	352,775	341,402	356,716	
	133,404	3,176	42	0/6	–	50	349,750	347,293	352,628	
	63,166	1,462	47	0/6	–	84	351,805	346,665	357,021	
						99	354,396	337,365	372,097	
Swine	858,262	6,131	142	6/6	2(4), 48(2)	1	174,558	73,193	416,303	6.87
	662,230	4,834	137	5/6	2(5)	16	272,801	183,332	405,933	
	464,444	7,491	62	5/6	1(4), 2(1)	30	319,368	250,207	407,484	
	437,900	7,830	62	6/6	1(6)	50	380,753	327,295	436,276	
	394,480	6,363	62	2/6		84	531,421	361,889	773,959	
	373,002	6,016	62	4/6	1(4)	99	830,513	356,216	1,936,330	
	349,440	5,636	62	0/6	–					
	293,822	3,194	92	3/6	1(3)					
	279,106	6,645	42	0/6	–					
Goat	662,230	4,834	137	6/6	2(6)	1	371,623	346,747	398,284	44.56
	437,900	7,830	62	6/6	1(4), 2(2)	16	387,519	375,086	300,364	
	394,480	6,363	62	2/6	21(1), 48(1)	30	393,291	376,671	410,546	
	349,440	5,636	62	0/6	–	50	399,831	382,689	417,741	
					–	84	412,535	406,268	418,899	
						99	430,181	393,738	469,998	
Rabbit	464,444	7,491	62	6/6	1(6)	1	13,042	2,630	64,680	2.46
	349,400	5,635	62	5/6	1(3), 18(2)	16	45,292	20,499	100,074	
	110,242	2,625	42	2/6	1(1), 504(1)	30	70,287	39,707	124,420	
	109,602	2,610	42	3/6	24(2), 168(1)	50	114,756	71,537	184,085	
	65,002	2,408	27	2/6	480(2)	84	290,753	125,366	674,321	
	39,112	3,259	12	1/6	120(1)	99	1,009,741	192,350	5,300,631	
	11,626	1,453	8	0/6	–					

Table A-3. (Contd)

Species	Ct	Concentration	Exposure time	Mortality fraction	Times to death	Bliss Statistical Analysis				
						Mortality	LD	Lower limit	Upper limit	Slope
	mg min/cu m	mg/cu m	min		hr	%				
Rat	464,444	7,491	62	20/20	1(20)	1	63,032	26,574	149,508	4.00
	349,400	5,635	62	19/20	1(10), 8(9)	16	135,555	92,619	198,396	
	279,106	6,645	42	3/20	20(3)	30	177,624	140,425	224,677	
	110,242	2,624	42	3/20	1(1), 20(2)	50	240,130	201,788	285,757	
	109,602	2,610	42	1/20	1(1)	84	425,379	271,702	665,975	
	65,002	2,408	27	0/20	–	99	914,809	358,669	2,333,285	
	56,436	1,764	32	1/20	168(1)					
	39,112	3,259	12	0/20	–					
Guinea pig	349,400	5,635	62	20/20	1(17), 18(2), 48(1)	1	26,472	10,242	68,420	2.82
	279,106	6,645	42	8/20	1(2), 20(6)	16	78,420	54,484	112,871	
	110,242	2,625	42	7/20	1(3), 20(2), 336(2)	50	176,448	134,494	231,499	
	109,602	2,610	42	7/20	18(6), 48(1)	84	397,015	202,164	779,670	
	65,002	2,408	27	3/20	480(3)	99	1,176,111	324,649	4,260,717	
	56,436	1,764	32	1/20	18(1)					
	39,112	3,259	12	0/20						
All rodents (rat and guinea pig)	–	–	–	–	–	1	37,812	17,531	81,555	3.16
						16	99,907	74,725	133,576	
						30	140,781	120,107	165,013	
						50	206,393	172,137	247,466	
						84	426,375	255,825	710,625	
						99	1,126,575	413,635	3,068,332	
All non rodents (monkey, dog, goat, swine, rabbit)	–	–	–	–	–	1	2,899	156	53,997	1.33
						16	28,807	6,995	118,636	
						30	64,789	26,343	159,346	
						50	160,013	106,352	240,751	
						84	888,806	336,847	2,345,215	
						99	8,831,180	751,951	103,716,570	
All species combined	–	–	–	–	–	1	18,529	7,181	47,811	2.20
						16	74,628	50,344	110,625	
						30	122,030	98,225	151,605	
						50	211,205	182,107	244,952	
						84	597,736	362,525	985,557	
						99	2,407,420	835,084	6,940,226	

* Figures in parentheses indicate number of animals dying.

APPENDIX B

SPECIFICATION FOR DYE IN RED SMOKE

MIL-D-3284C
24 June 1971
SUPERSEDING
MIL-D-003284B(MU)
29 May 1968
MIL-D-3284A
15 July 1963

MILITARY SPECIFICATION

DYE, DISPERSE RED 9

This specification is mandatory for use by all Departments and Agencies of the Department of Defense.

1. SCOPE

1.1 This specification covers Disperse Red 9 dye, chemically known as 1-methylaminoanthraquinone.

2. APPLICABLE DOCUMENTS

2.1 Government documents. The following documents of the issue in effect on date of invitation for bids or request for proposal form a part of this specification to the extent specified herein.

SPECIFICATIONS

FEDERAL

L-P-378 - Plastic Sheet and Film (Polyolefin).
RR-S-366 - Sieve, Test.

MILITARY

MIL-D-3464 - Desiccants, Activated, Bagged, Packaging Use and Static Dehumidification.

FSC 6820

STANDARDS

MILITARY

MIL-STD-105 - Sampling Procedures and Tables for Inspection by Attributes.
MIL-STD-129 - Marking for Shipment and Storage.
MIL-STD-147 - Palletized and Containerized Unit Loads, 40" x 48" Pallets, Skids, Runners, or Pallet-Type Base.

(Copies of specifications, standards, drawings, and publications required by suppliers in connection with specific procurement functions should be obtained from the procuring activity or as directed by the contracting officer.)

2.2 Other publications. The following documents form a part of this specification to the extent specified herein. Unless otherwise indicated, the issue in effect on date of invitation for bids or request for proposal shall apply.

UNIFORM FREIGHT CLASSIFICATION RULES

(Application for copies should be addressed to the Uniform Classification Committee, 202 Union Station, Chicago, Illinois 60606.)

NATIONAL MOTOR FREIGHT CLASSIFICATION RULES

(Application for copies should be addressed to the American Trucking Association, Inc., Attention: Tariff Order Section, 1616 P Street, N.W., Washington, D. C. 20036.)

AMERICAN SOCIETY FOR TESTING AND MATERIALS (ASTM) STANDARDS

D1193-66 - Reagent Water.
D1895-65T - Apparent Density, Bulk Factor, and Pourability of Plastic Materials.

(Application for copies should be addressed to the American Society for Testing and Materials, 1916 Race Street, Philadelphia, Pennsylvania 19103.)

(Technical society and technical association specifications and standards are generally available for reference from libraries. They are also distributed among technical groups and using Federal agencies.)

3. REQUIREMENTS

3.1 Chemical and physical characteristics. Disperse Red 9 dye shall conform to the chemical and physical characteristics of table I when tested as specified therein.

Table I. Chemical and physical characteristics

Characteristic	Requirement	Test paragraph
Purity, percent by weight, minimum	90	4.2.4.1
Volatile matter, percent by weight, maximum	2.5	4.2.4.2
Particle size, percent by weight passing:		4.2.4.3
260 microns (No. 60), minimum	97	
149 microns (No. 100), minimum	90	
74 microns (No. 200), minimum	70	
Apparent density, grams per milliliter (dry basis)	0.35 ± 0.15	4.2.4.4

4. QUALITY ASSURANCE PROVISIONS

4.1 Responsibility for inspection. Unless otherwise specified in the contract or purchase order, the supplier is responsible for the performance of all inspection requirements as specified herein. Except as otherwise specified in the contract or order, the supplier may use his own or any other facilities suitable for the performance of the inspection requirements specified herein, unless disapproved by the Government. The Government reserves the right to perform any of the inspections set forth in the specification where such inspections are deemed necessary to assure supplies and services conform to specified requirements.

4.2 Quality conformance inspection.

4.2.1 Lotting. A lot shall consist of the Disperse Red 9 dye offered for acceptance at one time which has been produced by one manufacturer, at one plant, from the same materials, and under essentially the same manufacturing conditions provided the operation is continuous. In the event the process is a batch operation, each batch shall constitute a lot (see 6.3).

4.2.2 Sampling.

4.2.2.1 For examination of preparation for delivery. Sampling for examination of preparation for delivery shall be conducted in accordance with MIL-STD-105.

4.2.2.2 For test. Three representative specimens of approximately 1/4 pound each shall be randomly removed from the lot or batch of dye offered for acceptance and shall be placed in separate clean, dry containers labeled to identify the lot represented.

4.2.3 Inspection procedure.

4.2.3.1 For examination of preparation for delivery. The sample unit shall be one filled and closed shipping container, ready for shipment. Sample containers and the preparation for delivery thereof shall be examined for the following defects using an AQL of 2.5 percent defective:

(a) Contents per container not as specified
(b) Container not as specified
(c) Polyethylene liner or closure thereof not as specified (level B only)
(d) Container closure not as specified
(e) Container damaged or leaking
(f) Desiccant not as specified or missing (level B only)
(g) Marking incorrect, missing, or illegible
(h) Palletization not as specified

4.2.3.2 For test. Each specimen taken in 4.2.2.2 shall be tested as specified in 4.2.4. Failure of any test by any specimen shall be cause for rejection of the lot represented.

4.2.4 Tests. Water in accordance with ASTM D1193 and reagent grade chemicals shall be used throughout the tests. Where applicable, blank determinations shall be run and corrections applied where significant. Tests shall be conducted as follows:

4.2.4.1 Purity. Prepare and measure the absorbance of a standard Disperse Red 9 dye solution (see 6.4) and specimen solution as follows: Weigh to the nearest milligram (mg) approximately 0.400 gram (g) of the dye and quantitatively transfer to a 500-milliliter (ml) volumetric flask using small amounts of isopropyl alcohol for washing. Dissolve the specimen in approximately 200 ml of isopropyl alcohol, stirring and breaking up all lumps to facilitate solution. Dilute to 500 ml with isopropyl alcohol. Shake thoroughly to insure uniform mixing. Remove a 20-ml aliquot, transfer to a second 500-ml volumetric flask, dilute to 500 ml with isopropyl alcohol, and mix thoroughly. Using a suitable spectrophotometer, read the absorbance value of the more dilute solution at 500 $\pm$ 2 millimicrons. Use the isopropyl alcohol used in preparing the solution as the reference liquid in the spectrophotometer. Cell spacers or variable path length cells may be used in lieu of the prescribed dilution procedures. Calculate the percent purity as follows:

$$\text{Percent purity} = \frac{ABC}{DE}$$

where: A = Percent purity of standard,
B = Absorbance value of specimen,
C = Weight of standard in grams,
D = Absorbance value of standard, and
E = Weight of specimen in grams.

4.2.4.2 Volatile matter. Weigh to the nearest milligram approximately 5 g of the specimen in a tared, glass-stoppered weighing bottle. Remove the stopper and dry to constant weight at 70° to 75° C. Cool to room temperature in a desiccator and weigh. Calculate the percent volatile matter as follows:

$$\text{Percent volatile matter} = \frac{100(A - B)}{W}$$

where: A = Weight of specimen and stoppered bottle before heating in grams,
B = Weight of specimen and stoppered bottle after heating in grams, and
W = Weight of specimen in grams.

4.2.4.3 Particle size. Use sieves conforming to RR-S-366. Nest the sieves in order of decreasing mesh size (with the sieve of largest mesh on top) on a receiving pan. Weigh to the nearest 0.01 g approximately 10 g of the specimen and then use one of the following procedures:

(a) Dry method. Place the weighed specimen on the top sieve and brush the material with a camel's-hair brush until no more specimen passes through the sieve. Remove the sieve and weigh the material retained. Repeat this procedure with each of the other sieves. Calculate the percent material passing through each sieve.

(b) Wet method. Mix the weighed specimen with sufficient water in a beaker by stirring with a glass rod to produce a smooth paste. Carefully wash the thoroughly wetted specimen through the sieves. (The use of a wetting agent is permitted.) Dry the sieves in an oven at 70° to 75° C and weigh the material remaining on each sieve. Calculate the percent material passing through each sieve.

4.2.4.4 Apparent density. Determine apparent density in accordance with ASTM D1895, method A except that the specimen shall be dried as specified in 4.2.4.2 prior to testing.

5. PREPARATION FOR DELIVERY

5.1 Packing. Packing shall be level B or C as specified (see 6.2).

5.1.1 Level B. Uniform quantities of no less than 150 and no more than 300 pounds ± 1/4 percent of the marked net weight of dye shall be packed in a fiber drum conforming to rule 51, section 2 of the Uniform Freight Classification for a weight limit of over 225 but not over 300 pounds, with an aluminum barrier of 0.5 mil minimum thickness incorporated into one of the inner plies of the sidewall. Each drum shall be provided with a close fitting bag liner formed from polyethylene of 4 mils minimum thickness conforming to type I, grade and finish optional of L-P-378. Seams shall be completely heat sealed and shall meet the heat-seal strength requirements of L-P-378. The filled bag shall be closed by heat sealing, tying, or knotting. A minimum of eight units of desiccant conforming to MIL-D-3464 shall be placed on top of the closed liner. Drum closure shall be fully gasketed and shall form a tight seal between the rim and the top of the drum.

5.1.2 Level C. Uniform quantities of no less than 150 and no more than 300 pounds ± 1/4 percent of the marked net weight of dye shall be packed in containers which comply with the Uniform Freight Classification Rules, the National Motor Freight Classification Rules, or other carrier rules as applicable to the mode of transportation. Containers shall be capable of being stacked and of supporting superimposed loads during shipment and shall assure safe delivery to destination without damage to contents. Containers shall be acceptable for shipment at the most favorable rate of the applicable regulation provided that all requirements specified herein have been met.

5.2 Marking. Marking shall be in accordance with MIL-STD-129. In addition, each container shall be durably and legibly marked with contrasting letters and background to show the net weight of contents and the following information:

CAUTION

Avoid contact with skin or clothing.
In case of contact, flush with water.
Avoid breathing dust or fumes.
Use with adequate ventilation.

5.3 Palletization. Shipping containers shall be palletized in accordance with the applicable requirements of MIL-STD-147 except that the pallet shall be as specified in the contract or order (see 6.2).

6. NOTES

6.1 Intended use. Disperse Red 9 dye is intended for use in the manufacture of colored signaling smoke mixtures.

6.2 Ordering data. Procurement documents should specify the following:

(a) Title, number, and date of this specification.
(b) Level of packing required (see 5.1).
(c) Type of pallet required (see 5.3).

6.3 Batch. A batch is defined as that quantity of material which has been manufactured by some unit chemical process or subjected to some physical mixing operation intended to make the final product substantially uniform.

6.4 Standard dye. Standard dye for the purity determination may be obtained from Commanding Officer, Edgewood Arsenal, Quality Assurance Directorate, Edgewood Arsenal, Maryland 21010.

6.5 Significant places. For the purpose of determining conformance with this specification, an observed or calculated value should be rounded off "to the nearest unit" in the last right-hand place of figures used in expressing the limiting value, in accordance with the rounding-off method of the Recommended Practices for Designating Significant Places in Specified Limiting Values (ASTM E29).

6.6 Nomenclature. Disperse Red 9 dye is commercially known under various names such as Celanthrene Red Y. It is listed in the Colour Index under number CI60505.

Custodians:

Army - MU
Navy - AS

Review activities:

Army - MD, MU(FA)
Navy - AS, OS
DSA - GS

User activity:

Army - SM

Preparing activity:

Army - MU(EA)

Project No. 6820-0052

☆U.S. GOVERNMENT PRINTING OFFICE: 1971-714-156/276

APPENDIX C

SPECIFICATION FOR DYE IN YELLOW SMOKE (AND OTHERS)

MIL-D-0050029C(MU)
26 April 1968
USED IN LIEU OF
MIL-D-50029B
15 July 1963
SUPERSEDING
Interim Amendment 1 (MU)
7 July 1965

MILITARY SPECIFICATION

DYE, VAT YELLOW 4

This limited coordination Military specification has been prepared by Edgewood Arsenal based upon currently available technical information, but it has not been approved for promulgation as a coordinated revision of Military Specification MIL-D-50029B. It is subject to modification. However, pending its promulgation as a coordinated Military specification, it may be used in procurement.

1. SCOPE

1.1 This specification covers Vat Yellow 4 dye, chemically known as a dibenzpyrenequinone type dye.

2. APPLICABLE DOCUMENTS

2.1 Government documents. The following documents of the issue in effect on date of invitation for bids or request for proposal, form a part of this specification to the extent specified herein.

SPECIFICATIONS

FEDERAL

L-P-378 - Plastic Film (Polyethylene Thin Gage).
RR-S-366 - Sieve, Test.

FSC 6820

MILITARY

MIL-D-3464 - Desiccants, Activated, Bagged, Packaging Use and Static Dehumidification.

MIL-P-15011 - Pallets, Material Handling, Wood, Post Construction, 4-Way Entry.

STANDARDS

MILITARY

MIL-STD-129 - Marking for Shipment and Storage.
MIL-STD-147 - Palletized and Containerized Unit Loads, 40" x 48" 4-Way (Partial) Pallet Skids, Runners, or Pallet-Type Base.

(Copies of specifications, standards, drawings, and publications required by suppliers in connection with specific procurement functions should be obtained from the procuring activity or as directed by the contracting officer.)

2.2 Other publications. The following documents form a part of this specification to the extent specified herein. Unless otherwise indicated, the issue in effect on date of invitation for bids or request for proposal shall apply.

UNIFORM CLASSIFICATION COMMITTEE

Uniform Freight Classification

(Application for copies of these ratings, rules, and regulations should be addressed to Uniform Classification Committee, 202 Union Station, 516 West Jackson Boulevard, Chicago, Illinois 60606.)

AMERICAN SOCIETY FOR TESTING AND MATERIALS

ASTM Standards

D1193-66 - Reagent Water.

(Application for copies should be addressed to the American Society for Testing and Materials, 1916 Race Street, Philadelphia, Pennsylvania 19103.)

(Technical society and technical association specifications and standards are generally available for reference from libraries. They are also distributed among technical groups and using Federal agencies.)

3. REQUIREMENTS

3.1 Chemical and physical characteristics. Vat Yellow 4 dye shall conform to the chemical and physical characteristics of table I when tested as specified therein.

Table I. Chemical and physical characteristics

Characteristic	Requirement	Test paragraph
Purity, percent by weight, minimum	80	4.2.4.1
Volatile matter, percent by weight, maximum	1.0	4.2.4.2
Particle size, percent by weight passing:		
840 microns (No. 20), minimum	100	4.2.4.3
297 microns (No. 50), minimum	97	4.2.4.3
44 microns (No. 325), maximum	40	4.2.4.3
Percent "Marcol 52" (as anti-dusting agent)	2.0 + 0.5	4.2.4.4

4. QUALITY ASSURANCE PROVISIONS

4.1 Responsibility for inspection.

4.1.1 Supplier's responsibility. Unless otherwise specified in the contract or purchase order, the supplier is responsible for the performance of all inspection requirements as specified herein. Except as otherwise specified in the contract or order, the supplier may use his own or any other facilities suitable for the performance of the inspection requirements specified herein, unless disapproved by the Government. The Government reserves the right to perform any of the inspections set forth in the specification where such inspections are deemed necessary to assure supplies and services conform to specified requirements.

4.1.2 Objective evidence. The supplier shall provide objective evidence acceptable to the contracting officer that the requirements of section 5 for which specific inspection has not been provided in this specification have been satisfied.

4.2 Quality conformance inspection.

4.2.1 Lotting. A lot shall consist of the Vat Yellow 4 dye offered for acceptance at one time which has been produced by one manufacturer, at one plant, from the same materials, and under essentially the same manufacturing conditions provided the operation is continuous. In the event the process is a batch operation, each batch shall constitute a lot (see 6.3)

4.2.2 Sampling for test. Sampling shall be conducted in accordance with table II. A representative specimen of no less than 1/4 pound shall be removed from each container in the sample and placed in a separate clean, dry container labeled to identify the lot and container from which it was taken.

Table II. Sampling for test

Number of containers in lot or batch	Number of sample containers
2-25	2
26-150	3
151-1,200	5
1,201-7,000	8
7,001-20,000	10
over 20,000	20

4.2.3 Inspection procedure. Each sample specimen shall be tested as specified in 4.2.4. Failure of any test by any specimen shall be cause for rejection.

4.2.4 Tests. Water in accordance with ASTM D1193 and reagent grade chemicals shall be used throughout the tests. Where applicable, blank determinations shall be run and corrections applied where significant. Tests shall be conducted as follows:

4.2.4.1 Purity. Prepare a standard dye solution (see 6.4) and specimen solution as follows: Weigh to the nearest milligram 0.100 gram (g) of the dye and transfer quantitatively to a 500-ml volumetric flask. Dissolve in concentrated sulfuric acid and dilute to 500 ml with concentrated sulfuric acid. Mix thoroughly. Transfer a 10-ml aliquot to a 250-ml volumetric flask and dilute to 250 ml with concentrated sulfuric acid. Mix thoroughly. Transfer a portion of each solution to matched 1-centimeter cells of a spectrophotometer and obtain the absorbance (abs)

of each solution at 568 to 571 millimicrons using concentrated sulfuric acid in the reference cell. Calculate the percent purity as follows:

$$\text{Percent purity} = \frac{100 \text{ (abs of specimen at 568 to 571 millimicrons)}}{\text{(abs of standard at 568 to 571 millimicrons)}}$$

4.2.4.2 Volatile matter. Weigh to the nearest milligram approximately 5 g of the specimen in a tared, glass-stoppered weighing bottle. Remove the stopper and dry to constant weight at 70° to 75° C. Cool to room temperature in a desiccator and weigh. Calculate the percent volatile matter as follows:

$$\text{Percent volatile matter} = \frac{100(A-B)}{W}$$

where: A = Weight of specimen and stoppered bottle before heating in grams,
B = Weight of specimen and stoppered botttle after heating in grams, and
W = Weight of specimen in grams.

4.2.4.3 Particle size. Use sieves conforming to RR-S-366. Nest the sieves in order of decreasing mesh size (with the largest mesh sieve on top) on a receiving pan. Weigh to the nearest 0.1 g approximately 10 g of the specimen and then use one of the following procedures:

(a) Dry method. Place the weighed specimen on the top sieve and brush the material with a camel's-hair brush until no more specimen passes through the sieve. Remove the sieve and weigh the material retained. Repeat this procedure with each of the other sieves. Calculate the material passing through each sieve.

(b) Wet method. Mix the weighed specimen with sufficient water in a beaker by stirring with a glass rod to produce a smooth paste. Carefully wash the thoroughly wetted specimen through the sieves. (The use of a wetting agent is permitted.) Dry the sieves in an oven at 70° to 75° C and weigh the material remaining on each sieve. Calculate the percent material passing through each sieve.

4.2.4.4 Anti-dusting agent ("Marcol 52").

(a) Reference standard. Prepare a series of six standard "Marcol 52" solutions in carbon tetrachloride containing 0.20 to 0.60 g of "Marcol 52" per 100 ml of carbon tetrachloride. (This is equivalent to 1.0 to 3.0 percent "Marcol 52" per 20 g of specimen.) Determine

the absorbance of the standard solutions at 2,310 or 3,410 ± 2 millimicrons using an infra-red spectrophotometer which has been balanced at zero or at a predetermined setting using a carbon tetrachloride blank. Prepare a calibration chart of absorbance versus percent "Marcol 52" in a 20-g specimen.

(b) Preparation of specimen. Weigh 20.000 g of the specimen into a 250-ml beaker. Add 50 ml of carbon tetrachloride and agitate for at least 1/2 hour (the specimen will not dissolve). Filter with suction. Wash the funnel and precipitate with 20 to 30 ml of carbon tetrachloride. Quantitatively transfer the filtrate to a 100-ml volumetric flask and dilute to 100 ml with carbon tetrachloride.

(c) Procedure. Determine the absorbance of the specimen solution prepared as specified in (b) at 2,310 or 3,410 ± 2 millimicrons using the same instrument, balancing, and wave length as was used in the standard solution measurements. Calculate the percent "Marcol 52" from the calibration chart prepared as specified in (a).

5. PREPARATION FOR DELIVERY

5.1 Packing. Packing shall be level B or C as specified (see 6.2).

5.1.1 Level B. Uniform quantities of no less than 150 and no more than 300 pounds ± 1/4 percent of the marked net weight of dye shall be packed in a fiber drum conforming to rule 51, section 2 of the Uniform Freight Classification with an aluminum barrier of 0.5 mil minimum thickness incorporated into one of the inner plies of the sidewall. Each drum shall be provided with a close fitting bag liner formed from polyethylene of 4 mils minimum thickness conforming to type I, grade and finish optional of L-P-378. Seams shall be completely heat sealed and shall meet the heat-seal requirements of L-P-378. The filled bag shall be closed by heat sealing, tying, or knotting. A minimum of eight units of desiccant conforming to MIL-D-3464 shall be placed on top of the closed liner. Drum closure shall be fully gasketed and shall form a tight seal between the rim and the top of the drum.

5.1.2 Level C. Quantities of Vat Yellow 4 dye as specified shall be packed to provide adequate protection against contamination, deterioration, and damage and to insure carrier acceptance and safe delivery to the first domestic destination. Containers shall be in compliance with Uniform Freight Classification rules or the regulations of other common carriers applicable to the mode of transportation (see 6.2).

5.2 Marking. In addition to the marking specified in 5.2.1 and any special marking required by the contract or order, containers shall be marked in accordance with MIL-STD-129 (see 6.2).

5.2.1 Special marking. Each container shall be durably and legibly marked with contrasting letters and background as follows:

CAUTION

Avoid skin contact.
Avoid breathing dust or fumes.
Use with adequate ventilation.

5.3 Palletization. When specified in the contract or order, shipping containers shall be palletized in accordance with the applicable requirements of MIL-STD-147 utilizing the hardwood, 4-way, 40- by 48-inch, double-wing pallet of MIL-P-15011 (see 6.2).

6. NOTES

6.1 Intended use. Vat Yellow 4 dye is intended for use in the manufacture of colored signalling smoke mixtures.

6.2 Ordering data. Procurement documents should specify the following:

(a) Title, number, and date of this specification.
(b) Level of packing required.
(c) Quantity required for level C packing.
(d) Special marking other than 5.2.1, if required.
(e) Palletization, if required.

6.3 Batch. A batch is defined as that quantity of material which has been manufactured by some unit chemical process and subjected to some physical mixing operation intended to make the final product substantially uniform.

6.4 Standard dye. Standard dye for the purity determination may be obtained form Commanding Officer, Edgewood Arsenal, Quality Assurance Directorate, Edgewood Arsenal, Maryland 21010.

6.5 Nomenclature. Indanthrene Golden Yellow GK is a typical commercial name for Vat Yellow 4 dye. It is listed in the Colour Index under number CI59100. Additional commercial names may be found on page 2430, Volume 2 of the Colour Index.

6.6 Anti-dusting agent. "Marcol 52" is a highly refined petroleum oil obtainable from the Humble Oil Company.

6.7 Significant places. For the purpose of determining conformance with this specification, an observed or calculated value shall be rounded off "to the nearest unit" in the last right-hand place of figures used in expressing the limiting value, in accordance with the rounding-off method of the Recommended Practices for Designating Significant Places in Specified Limiting Values (ASTM E29).

Custodian:

Army - MU

Preparing activity:

Army - MU(EA)

Project No. 6810-A042

☆ U. S. GOVERNMENT PRINTING OFFICE: 1968-301-519/5778

APPENDIX D

SPECIFICATIONS FOR DYE USED IN YELLOW AND GREEN SMOKES

MIL-D-0050074C(MU)
9 May 1968
USED IN LIEU OF
MIL-D-50074B
1 July 1963

MILITARY SPECIFICATION

DYE, BENZANTHRONE

This limited coordinated Military specification has been prepared by Edgewood Arsenal based upon currently available technical information, but it has not been approved for promulgation as a coordinated revision of Military Specification MIL-D-50074B. It is subject to modification. However, pending its promulgation as a coordinated Military specification, it may be used in procurement.

1. SCOPE

1.1 This specification covers benzanthrone dye, chemically known as 1,9-benz-10-anthrone.

2. APPLICABLE DOCUMENTS

2.1 Government documents. The following documents of the issue in effect on date of invitation for bids or request for proposal, form a part of this specification to the extent specified herein.

SPECIFICATIONS

FEDERAL

L-P-378 - Plastic Film (Polyethylene Thin Gage).
RR-S-366 - Sieve, Test.

MILITARY

MIL-D-3464 - Desiccants, Activated, Bagged, Packaging Use and Static Dehumidification.
MIL-P-15011 - Pallets, Material Handling, Wood, Post Construction, 4-Way Entry.

FSC 6820

STANDARDS

MILITARY

MIL-STD-129 - Marking for Shipment and Storage.
MIL-STD-147 - Palletized and Containerized Unit Loads, 40" x 48" 4-Way (Partial) Pallet Skids, Runners, or Pallet-Type Base.

(Copies of specifications, standards, drawings, and publications required by suppliers in connection with specific procurement functions should be obtained from the procuring activity or as directed by the contracting officer.)

2.2 Other publications. The following documents form a part of this specification to the extent specified herein. Unless otherwise indicated, the issue in effect on date of invitation for bids or request for proposal shall apply.

UNIFORM CLASSIFICATION COMMITTEE

Uniform Freight Classification

(Application for copies of these ratings, rules, and regulations should be addressed to Uniform Classification Committee, 202 Union Station, 516 West Jackson Boulevard, Chicago, Illinois 60606.)

AMERICAN SOCIETY FOR TESTING AND MATERIALS

ASTM Standards

D1193-66 - Reagent Water.

(Application for copies should be addressed to the American Society for Testing and Materials, 1916 Race Street, Philadelphia, Pennsylvania 19103.)

(Technical society and technical association specifications and standards are generally available for reference from libraries. They are also distributed among technical groups and using Federal agencies.)

3. REQUIREMENTS

3.1 Chemical and physical characteristics. Benzanthrone dye shall conform to the chemical and physical characteristics of table I when tested as specified therein.

Table I. Chemical and physical characteristics

Characteristic	Requirement	Test paragraph
Purity, percent by weight, minimum	77	4.2.4.1
Volatile matter, percent by weight, maximum	1.0	4.2.4.2
Particle size, percent by weight passing:		
840 microns (No. 20), minimum	100	4.2.4.3
297 microns (No. 50), minimum	97	4.2.4.3
44 microns (No. 325), maximum	40	4.2.4.3
Percent "Marcol 52" (as anti-dusting agent)	2.0 ± 0.5	4.2.4.4

4. QUALITY ASSURANCE PROVISIONS

4.1 Responsibility for inspection.

4.1.1 Supplier's responsibility. Unless otherwise specified in the contract or purchase order, the supplier is responsible for the performance of all inspection requirements as specified herein. Except as otherwise specified in the contract or order, the supplier may use his own or any other facilities suitable for the performance of the inspection requirements specified herein, unless disapproved by the Government. The Government reserves the right to perform any of the inspections set forth in the specification where such inspections are deemed necessary to assure supplies and services conform to specified requirements.

4.1.2 Objective evidence. The supplier shall provide objective evidence acceptable to the contracting officer that the requirements of section 5 for which specific inspection has not been provided in this specification have been satisfied.

4.2 Quality conformance inspection.

4.2.1 Lotting. A lot shall consist of the benzanthrone dye offered for acceptance at one time which has been produced by one manufacturer, at one plant, from the same materials, and under essentially the same manufacturing conditions provided the operation is continuous. In the event the process is a batch operation, each batch shall constitute a lot (see 6.3).

4.2.2 Sampling for test. Sampling shall be conducted in accordance with table II. A representative specimen of no less than 1/2 pound shall be removed from each container in the sample and placed in a separate clean, dry container labeled to identify the lot and container from which it was taken.

Table II. Sampling for test

Number of containers in lot or batch	Number of sample containers
2-25	2
26-150	3
151-1,200	5
1,201-7,000	8
7,001-20,000	10
over 20,000	20

4.2.3 Inspection procedure. Each sample specimen shall be tested as specified in 4.2.4. Failure of any test by any specimen shall be cause for rejection.

4.2.4 Tests. Water in accordance with ASTM D1193 and reagent grade chemicals shall be used throughout the tests. Where applicable, blank determinations shall be run and corrections applied where significant. Tests shall be conducted as follows:

4.2.4.1 Purity. Prepare a standard benzanthrone dye solution (see 6.4) and specimen solution as follows: Weigh to the nearest milligram (mg) approximately 0.350 gram (g) of the dye, which has been previously dried to constant weight at 70° to 75° C, and transfer quantitatively to a 500-milliliter (ml) volumetric flask. Add approximately 250 ml of toluene and thoroughly mix to dissolve the benzanthrone. Dilute with toluene to 500 ml and again thoroughly mix. Transfer a 5-ml aliquot to a 200-ml volumetric flask, dilute to 200 ml with toluene and thoroughly mix. Using a suitable spectrophotometer, measure the absorbance of the more

dilute solution of standard dye and the more dilute solution of specimen at 388 ± 2 millimicrons. Use the toluene used for preparing the solutions as the reference liquid in the spectrophotometer. Calculate the percent purity as follows:

$$\text{Percent purity} = \frac{100 \text{ (absorbance value of specimen)}}{\text{(absorbance value of standard)}}$$

4.2.4.2 Volatile matter. Weigh to the nearest milligram approximately 5 g of the specimen in a tared, glass-stoppered weighing bottle. Remove the stopper and dry to constant weight at 70° to 75° C. Cool to room temperature in a desiccator and weigh. Calculate the percent volatile matter as follows:

$$\text{Percent volatile matter} = \frac{100(A-B)}{W}$$

where: A = Weight of specimen and stoppered bottle before heating in grams,
B = Weight of specimen and stoppered bottle after heating in grams, and
W = Weight of specimen in grams.

4.2.4.3 Particle size. Use sieves conforming to RR-S-366. Nest the sieves in order of decreasing mesh size (with the sieve of largest mesh on top) on a receiving pan. Weigh to the nearest 0.1 g approximately 10 g of the specimen and then use one of the following procedures:

(a) Dry method. Place the weighed specimen on the top sieve and brush the material with a camel's-hair brush until no more specimen passes through the sieve. Remove the sieve and weigh the material retained. Repeat this procedure with each of the other sieves. Calculate the percent material passing through each sieve.

(b) Wet method . Mix the weighed specimen with sufficient water in a beaker by stirring with a glass rod to produce a smooth paste. Carefully wash the thoroughly wetted specimen through the sieves. (The use of a wetting agent is permitted.) Dry the sieves in an oven at 70° to 75° C and weigh the material remaining on each sieve. Calculate the percent material passing through each sieve.

4.2.4.4 Anti-dusting agent ("Marcol 52").

(a) Reference standard. Prepare a series of six standard "Marcol 52" solutions in carbon tetrachloride containing 0.20 to 0.60 g

of "Marcol 52" per 100 ml of carbon tetrachloride. (This is equivalent to 1.0 to 3.0 percent "Marcol 52" per 20 g of specimen.) Determine the absorbance of the standard solutions at 2,310 or 3,410 ± 2 millimicrons using an infra-red spectrophotometer which has been balanced at zero or at a predetermined setting using a carbon tetrachloride blank. Prepare a calibration chart of absorbance versus percent "Marcol 52" in a 20-g specimen.

(b) Preparation of specimen. Weigh 20.000 g of the specimen into a 150-ml beaker. Add 50 ml of carbon tetrachloride and agitate for at least 1/2 hour (the specimen will not dissolve). Filter with suction. Wash the funnel and precipitate with 25 to 30 ml of carbon tetrachloride. Quantitatively transfer the filtrate to a 100-ml volumetric flask and dilute to 100 ml with carbon tetrachloride.

(c) Procedure. Determine the absorbance of the specimen solution prepared as specified in (b) at 2,310 or 3,410 ± 2 millimicrons using the same instrument and balancing as was used in the standard solution tests. Calculate the percent "Marcol 52" from the calibration chart prepared as specified in (a).

5. PREPARATION FOR DELIVERY

5.1 Packing. Packing shall be level B or C as specified (see 6.2).

5.1.1 Level B. Uniform quantities of no less than 150 and no more than 300 pounds ± 1/4 percent of the marked net weight of benzanthrone dye shall be packed in a fiber drum conforming to rule 51, section 2 of the Uniform Freight Classification with an aluminum barrier of 0.5 mil minimum thickness incorporated into one of the inner plies of the sidewall. Each drum shall be provided with a close fitting bag liner formed from polyethylene of 4 mils minimum thickness conforming to type I, grade and finish optional of L-P-378. Seams shall be completely heat sealed and shall meet the heat-seal requirements of L-P-378. The filled bag shall be closed by heat sealing, tying, or knotting. A minimum of eight units of desiccant conforming to MIL-D-3464 shall be placed on top of the closed liner. Drum closure shall be fully gasketed and shall form a tight seal between the rim and the top of the drum.

5.1.2 Level C. Quantities of benzanthrone dye as specified shall be packed to provide adequate protection against contamination, deterioration, and damage and to insure carrier acceptance and safe delivery to the first domestic destination, Containers shall be in compliance with Uniform Freight Classification rules or the regulations of other common carriers applicable to the mode of transportation (see 6.2).

5.2 Marking. In addition to the marking specified in 5.2.1 and any special marking required by the contract or order, containers shall be marked in accordance with MIL-STD-129 (see 6.2).

5.2.1 Special marking. Each container shall be durably and legibly marked with contrasting letters and background as follows:

CAUTION

Causes severe irritation to some people.
Avoid contact with skin or clothing.
In case of contact, flush with water.
Wash contaminated clothing before re-use.
Individuals sensitive to this product should not continue to work w. it.

5.3 Palletization. When specified in the contract or order, shipping containers shall be palletized in accordance with the applicable requirements of MIL-STD-147 utilizing the hardwood, 4-way, 40-by 48-inch, double-wing pallet of MIL-P-15011 except that the strapping shall have a minimum width of 1.25 inch and a minimum thickness of 0.035 inch (see 6.2).

6. NOTES

6.1 Intended use. Benzanthrone dye is intended for use in the manufacture of colored signaling smoke mixtures.

6.2 Ordering data. Procurement documents should specify the following:

(a) Title, number, and date of this specification.
(b) Level of packing required.
(c) Quantity required for level C packing.
(d) Special marking other than 5.2.1, if required.
(e) Palletization, if required.

6.3 Batch. A batch is defined as that quantity of material which has been manufactured by some unit chemical process and subjected to some physical mixing operation intended to make the final product substantially uniform.

6.4 Standard dye. Standard dye for the purity determination may be obtained from Commanding Officer, Edgewood Arsenal, Quality Assurance Directorate, Edgewood Arsenal, Maryland 21010.

6.5 Anti-dusting agent. "Marcol 52" is a highly refined petroleum oil obtainable from the Humble Oil and Refining Company.

6.6 Significant places. For the purpose of determining conformance with this specification, an observed or calculated value shall be rounded off "to the nearest unit" in the last right-hand place of figures used in expressing the limiting value, in accordance with the rounding-off method of the Recommended Practices for Designating Significant Places in Specified Limiting Values (ASTM E29).

Custodian:

Army - MU

Preparing activity:

Army - MU(EA)

Project No. 6820-A043

☆ U. S. GOVERNMENT PRINTING OFFICE: 1968-301-519/5994

APPENDIX E

SPECIFICATIONS FOR DYE USED IN GREEN SMOKE

MIL-D-003277B(MU)
26 March 1968
USED IN LIEU OF
MIL-D-3277A
25 May 1962
SUPERSEDING
Interim Amendment 1(MU)
9 May 1966

MILITARY SPECIFICATION

DYE, SOLVENT GREEN 3

(FOR GREEN SMOKE MIXTURES)

This limited coordination Military specification has been prepared by Edgewood Arsenal based upon currently available technical information, but it has not been approved for promulgation as a coordinated revision of Military Specification MIL-D-3277A. It is subject to modification. However, pending its promulgation as a coordinated Military specification, it may be used in procurement.

1. SCOPE

1.1 This specification covers Solvent Green 3 dye, chemically known as 1,4-di-p-toluidinoanthraquinone.

2. APPLICABLE DOCUMENTS

2.1 Government documents. The following documents of the issue in effect on date of invitation for bids or request for proposal, form a part of this specification to the extent specified herein.

SPECIFICATIONS

FEDERAL

L-P-378 - Plastic Film (Polyethylene Thin Gage).
RR-S-366 - Sieve, Test.

MILITARY

MIL-D-3464 - Desiccants, Activated, Bagged, Packaging Use and Static Dehumidification.
MIL-P-15011 - Pallets, Material Handling, Wood, Post Construction, 4-Way Entry.

STANDARDS

MILITARY

MIL-STD-129 - Marking for Shipment and Storage.
MIL-STD-147 - Palletized and Containerized Unit Loads, 40" x 48" 4-Way (Partial) Pallet Skids, Runners, or Pallet-Type Base.

(Copies of specifications, standards, drawings, and publications required by suppliers in connection with specific procurement functions should be obtained from the procuring activity or as directed by the contracting officer.)

2.2 Other publications. The following documents form a part of this specification to the extent specified herein. Unless otherwise indicated, the issue in effect on date of invitation for bids or request for proposal shall apply.

UNIFORM CLASSIFICATION COMMITTEE

Uniform Frieght Classification

(Application for copies of these ratings, rules and regulations should be addressed to Uniform Classification Committee, 202 Union Station, 516 West Jackson Boulevard, Chicago, Illinois 60606.)

AMERICAN SOCIETY FOR TESTING AND MATERIALS

ASTM Standards

D1193-66 - Reagent Water
D1895-65T - Apparent Density, Bulk Factor, and Pourability of Plastic Materials.

(Application for copies should be addressed to the American Society for Testing and Materials, 1916 Race Street, Philadelphia, Pennsylvania 19103.)

(Technical society and technical association specifications and standards are generally available for reference from libraries. They are also distributed among technical groups and using Federal agencies.)

3. REQUIREMENTS

3.1 Chemical and physical characteristics. Solvent Green 3 dye shall conform to the chemical and physical characteristics of table I when tested as specified therein.

Table I. Chemical and physical characteristics

Characteristic	Requirement	Test paragraph
Purity, dry basis, percent by wt, minimum	90	4.2.4.1
Volatile matter, percent by wt, maximum	2.5	4.2.4.2
Particle size, percent by wt passing:		
840 microns (No. 20), minimum	100	4.2.4.3
297 microns (No. 50), minimum	97	4.2.4.3
44 microns (No. 325), maximum	40	4.2.4.3
Apparent density, grams per milliliter, minimum (dry basis)	0.38	4.2.4.4

4. QUALITY ASSURANCE PROVISIONS

4.1 Responsibility for inspection.

4.1.1 Supplier's responsibility. Unless otherwise specified in the contract or purchase order, the supplier is responsible for the performance of all inspection requirements as specified herein. Except as otherwise specified in the contract or order, the supplier may utilize his own or any other facilities suitable for the performance of the inspection requirements specified herein, unless disapproved by the Government. The Government reserves the right to perform any of the inspections set forth in the specification where such inspections are deemed necessary to assure supplies and services conform to specified requirements.

4.1.2 Objective evidence. The supplier shall provide objective evidence acceptable to the contracting officer that the requirements of section 5 for which specific inspection has not been provided in this specification have been satisfied.

4.2 Quality conformance inspection.

4.2.1 Lotting. A lot shall consist of the Solvent Green 3 dye offered for acceptance at one time which has been produced by one manufacturer, at one plant, from the same materials, and under essentially the same manufacturing conditions provided the operation is continuous. In the event the process is a batch operation, each batch shall constitute a lot (see 6.3).

4.2.2 Sampling for test. Sampling shall be conducted in accordance with table II. A representative specimen of no less than 1/4 pound shall be removed from each container in the sample and placed in a separate clean, dry container labeled to identify the lot and container from which it was taken.

Table II. Sampling for test

Number of containers in lot or batch	Number of sample containers
2-25	2
26-150	3
151-1,200	5
1,201-7,000	8
7,001-20,000	10
over 20,000	20

4.2.3 Inspection procedure. Each sample specimen shall be tested as specified in 4.2.4. Failure of any test by any specimen shall be cause for rejection.

4.2.4 Tests. Water in accordance with ASTM D1193 and reagent grade chemicals shall be used throughout the tests. Where applicable, blank determinations shall be run and corrections applied where significant. Tests shall be conducted as follows:

4.2.4.1 Purity. Prepare and measure the absorbance of a standard Solvent Green 3 dye solution (see 6.4) and a specimen solution as follows: Transfer 0.301 gram (g) of the dye, which has been dried to constant weight at 70° to 75° C as specified in 4.2.4.2, to a 500-milliliter volumetric flask, using small quantities of benzene to rinse the weighing container or paper. Dissolve in about 200 ml of benzene, stirring and breaking up all lumps to facilitate solution. Dilute to 500 ml with benzene. Shake the flask thoroughly to insure uniform mixing. Transfer a 20-ml aliquot to a second 500-ml volumetric flask, dilute to 500 ml with benzene, and mix thoroughly. Measure the absorbance of the solution at 642 millimicrons, using a suitable spectrophotometer, 1-centimeter light path cells, and benzene as the reference solution. Calculate the percent purity as follows:

$$\text{Percent purity} = \frac{100\ (\text{Absorbance value of specimen})}{\text{Absorbance value of standard}}$$

4.2.4. Volatile matter. In a tared, glass-stoppered weighing bottle, weigh to the nearest milligram approximately 5 g of the specimen. Remove the stopper and dry to constant weight in an oven at 70° to 75° C. Cool in a desiccator and weigh. Calculate percent volatile matter as follows:

$$\text{Percent volatile matter} = \frac{100\ (A-B)}{A}$$

where: B = Weight of residue in grams and
A = Weight of specimen in grams.

4.2.4.3 Particle size. Use sieves conforming to RR-S-366. Nest the sieves in order of decreasing mesh size (with the largest mesh sieve on top) on a receiving pan. Weigh to the nearest 0.1 g approximately 10 g of the specimen and then use one of the following procedures:

(a) Dry method. Place the weighed specimen on the top sieve and brush the material with a camel's-hair brush until no more specimen passes through the sieve. Remove the sieve and weigh the material retained. Repeat this procedure with each of the other sieves. Calculate the material passing through each sieve.

(b) Wet method. Mix the weighed specimen with sufficient water in a beaker by stirring with a glass rod to produce a smooth paste. Carefully wash the thoroughly wetted specimen through the sieves. (The use of a wetting agent is permitted.) Dry the sieves in an oven at 70° to 75° C and weigh the material remaining on each sieve. Calculate the percent material passing through each sieve.

4.2.4.4 Apparent density. Determine apparent density in accordance with ASTM D1895, method A except that the specimen shall be dried as specified in 4.2.4.2 prior to testing.

5. PREPARATION FOR DELIVERY

5.1 Packing. Packing shall be level B or C as specified (see 6.2).

5.1.1 Level B. Uniform quantities of no less than 150 and no more than 300 pounds ± 1/4 percent of the marked net weight of dye shall be packed in a fiber drum conforming to rule 51, section 2 of the Uniform Freight Classification with an aluminum barrier of 0.5 mil minimum thickness incorporated into one of the inner plies of the sidewall. Each drum shall be provided with a close fitting bag liner formed from polyethylene of 4 mils minimum thickness conforming to type I, grade and finish optional of L-P-378. Seams shall be completely heat sealed

and shall meet the heat-seal strength requirements of L-P-378. The filled bag shall be closed by heat sealing, typing, or knotting. A minimum of eight units of desiccant conforming to MIL-D-3646 shall be placed on top of the closed liner. Drum closure shall be fully gasketed and shall form a tight seal between the rim and top of the drum.

5.1.2 Level C. Quantities of Solvent Green 3 dye as specified shall be packed to provide adequate protection against contamination, deterioration, and damage and to insure carrier acceptance and safe delivery to the first domestic destination. Containers shall be in compliance with Uniform Freight Classification rules or the regulations of other common carriers applicable to the mode of transportation (see 6.2).

5.2 Marking. In addition to the marking specified in 5.2.1 and any special marking required by the contract or order, containers shall be marked in accordance with MIL-STD-129 (see 6.2).

5.2.1 Special marking. Each container shall be durably and legibly marked with contrasting letters and background as follows:

CAUTION

Avoid skin contact.
Use with adequate ventilation.

5.3 Palletization. When specified in the contract or order, shipping containers shall be palletized in accordance with the applicable requirements of MIL-STD-147 utilizing the hardwood, 4-way, 40- by 48-inch, double-wing pallet of MIL-P-15011 (see 6.2).

6. NOTES

6.1 Intended use. Solvent Green 3 dye is intended for use in green smoke mixtures.

6.2 Ordering data. Procurement documents should specify the following:

(a) Title, number, and date of this specification.
(b) Level of packing required.
(c) Quantity required for level C packing.
(d) Special marking other than 5.2.1, if required.
(e) Palletization, if required.

6.3 Batch. A batch is defined as that quantity of material which has been manufactured by some unit chemical process and subjected to some physical mixing operation intended to make the final product substantially uniform.

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6.4 Standard dye. Standard dye for the purity test may be obtained from Commanding Officer, Edgewood Arsenal, Quality Assurance Directorate, Edgewood Arsenal, Maryland 21010.

6.5 Significant places. For the purpose of determining conformance with this specification, an observed or claculated value shall be rounded off "to the nearest unit" in the last right-hand place of figures used in expressing the limiting value, in accordance with the rounding-off method of the Recommended Practices for Designating Significant Places in Specified Limiting Values (ASTM E29).

Custodian:

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SPECIFICATIONS FOR DYE USED IN VIOLET SMOKE

MIL-D-3691B
20 July 1970
SUPERSEDING
MIL-D-3691A
15 July 1963

MILITARY SPECIFICATION

DYE MIX, VIOLET

This specification is mandatory for use by all Departments and Agencies of the Department of Defense.

1. SCOPE

1.1 This specification covers a mixture of two anthraquinone dyes.

2. APPLICABLE DOCUMENTS

2.1 Government documents. The following documents of the issue in effect on date of invitation for bids or request for proposal, form a part of this specification to the extent specified herein.

SPECIFICATIONS

FEDERAL

L-P-378 - Plastic Sheet and Film (Polyolefin).
RR-S-366 - Sieve, Test.

MILITARY

MIL-D-3284 - Dye, Disperse Red 9.
MIL-D-3464 - Desiccants, Activated, Bagged, Packaging Use and Static Dehumidification.
MIL-D-3668 - Dye, 1,4-Diamino-2,3-Dihydroanthraquinone.

STANDARDS

MILITARY

MIL-STD-105 - Sampling Procedures and Tables for Inspection by Attributes.
MIL-STD-129 - Marking for Shipment and Storage.

FSC 6820

(Copies of specifications, standards, drawings, and publications required by suppliers in connection with specific procurement functions should be obtained from the procuring activity or as directed by the contracting officer.)

2.2 Other publications. The following documents form a part of this specification to the extent specified herein. Unless otherwise indicated, the issue in effect on date of invitation for bids or request for proposal shall apply.

UNIFORM FREIGHT CLASSIFICATION RULES

(Application for copies should be addressed to the Uniform Freight Classification Committee, 202 Union Station, 516 West Jackson Boulevard, Chicago, Illinois 60606.)

NATIONAL MOTOR FREIGHT CLASSIFICATION RULES

(Application for copies should be addressed to the National Classification Board, 1616 P Street, N.W., Washington, D.C. 20036.)

AMERICAN SOCIETY FOR TESTING AND MATERIALS (ASTM) STANDARDS

D1193-66 - Reagent Water.
D1895-67 - Apparent Density, Bulk Factor, and Pourability of Plastic Materials.

(Application for copies should be addressed to the American Society for Testing and Materials, 1916 Race Street, Philadelphia, Pennsylvania 19103.)

(Technical society and technical association specifications and standards are generally available for reference from libraries. They are also distributed among technical groups and using Federal agencies.)

3. REQUIREMENTS

3.1 Composition. Dye Mix, Violet shall be a uniformly blended mixture of dyes and shall conform to the composition of table I when tested as specified in 4.2.4.1.

3.2 Chemical and physical characteristics. Dye Mix, Violet shall conform to the chemical and physcial characteristics of table II when tested as specified therein.

Table I. Composition

Dye	Percent by weight
Dye, Disperse Red 9 conforming to MIL-D-3284	20 ± 2
Dye, 1,4-Diamino-2,3-dihydroanthraquinone conforming to MIL-D-3668	80 ± 2

Table II. Chemical and physical characteristics

Characteristic	Requirement	Test paragraph
Volatile matter, percent by weight, maximum	2.5	4.2.4.2
Particle size, minimum percent by weight passing:		4.2.4.3
250-micron (No. 60) sieve	97	
149-micron (No. 100) sieve	90	
74-micron (No. 200) sieve	70	
Apparent density, grams per milliliter	0.35 ± 0.15	4.2.4.4

4. QUALITY ASSURANCE PROVISIONS

4.1 Responsibility for inspection. Unless otherwise specified in the contract or purchase order, the supplier is responsible for the performance of all inspection requirements as specified herein. Except as otherwise specified in the contract or order, the supplier may use his own or any other facilities suitable for the performance of the inspection requirements specified herein, unless disapproved by the Government. The Government reserves the right to perform any of the inspections set forth in the specification where such inspections are deemed necessary to assure supplies and services conform to specified requirements.

4.2 Quality conformance inspection.

4.2.1 Lotting. A lot shall consist of the Dye Mix, Violet offered for acceptance at one time which has been produced by one manufacturer, at one plant, from the same materials, and under essentially the same manufacturing conditions provided the operation is continuous. In the event the process is a batch operation, each batch shall constitute a lot (see 6.3).

4.2.2 Sampling.

4.2.2.1 For examination of preparation for delivery. Sampling for examination of preparation for delivery shall be conducted in accordance with MIL-STD-105.

4.2.2.2 For test. Sampling for test shall be conducted in accordance with table III. A representative specimen of approximately 1/4 pound shall be removed from each sample shipping container and placed in a suitable clean, dry container labeled to identify the lot and container from which it was taken.

Table III. Sampling for test

Lot size, pounds	Number of sample shipping containers
3,000 or less	2
3,001 to 5,000	3
Over 5,000	5

4.2.3 Inspection procedure.

4.2.3.1 For examination of preparation for delivery. The sample unit shall be one filled and closed shipping container, ready for shipment. Sample containers and the preparation for delivery thereof shall be examined for the following defects using an AQL of 2.5 percent defective:

(a) Contents per container not as specified
(b) Container not as specified
(c) Polyethylene liner or closure thereof not as specified (level B only)
(d) Container closure not as specified
(e) Container damaged or leaking
(f) Desiccant not as specified or missing (level B only)
(g) Marking incorrect, missing, or illegible

4.2.3.2 For test. Each sample specimen taken in 4.2.2.2 shall be tested as specified in 4.2.4. Failure of any test by any specimen shall be cause for rejection of the lot represented.

4.2.4 Tests. Water in accordance with ASTM D1193 and reagent grade chemicals shall be used throughout the tests. Where applicable, blank determinations shall be run and corrections applied where significant. Tests shall be conducted as follows:

4.2.4.1 Composition.

(a) Preparation of standard curves. Prepare a standard curve of absorbance versus concentration for dye of known purity (see 6.4) conforming to MIL-D-3284 and dye of known purity (see 6.4) conforming to MIL-D-3668. Both dyes will dissolve in ethanol at the concentrations required; however, a slight warming on a steam bath may be necessary. Prepare solutions of the dye conforming to MIL-D-3668 in ethanol with concentrations ranging from 5 to 20 micrograms per milliliter (ml). Transfer a portion of the solution for each concentration to a spectrophotometer cell and measure the absorbance of each solution at 458 millimicrons (visible region) and at 314 millimicrons (ultraviolet region) using ethanol in the reference beam. Plot the absorbance values versus concentration for each of the wavelengths. A straight line should result. In the same manner, prepare solutions of the dye conforming to MIL-D-3284 in ethanol with concentrations ranging from 5 to 20 micrograms per milliliter and using ethanol in the reference beam, plot the absorbance values versus concentration for each of the solutions at 314 and 458 millimicrons. A straight line should result.

(b) Procedure. Prepare a solution of the specimen in ethanol having a concentration of 21 to 22 micrograms per milliliter. Place the specimen solution in a cuvet and place in the spectrophotometer. Use ethanol in the reference beam. Obtain spectral curves in both the visible and ultraviolet regions. Calculate the concentration of each dye as follows:

$$C_a = \frac{A_1K_{b2} - A_2K_{b1}}{B(K_{a1}K_{b2} - K_{a2}K_{b1})}$$

$$C_b = \frac{A_1K_{a2} - A_2K_{a1}}{B(K_{b1}K_{a2} - K_{b2}K_{a1})}$$

where: C = Concentration in grams per liter,
a = Dye conforming to pure dye component of MIL-D-3668,
b = Dye conforming to pure dye component of MIL-D-3284,
1 = Wavelength (314 millimicrons),
2 = Wavelength (458 millimicrons),
A = Absorbance read from spectral curve,
B = Cell length in centimeters (unity for a 1-centimeter cell), and
K = Absorbance value divided by solution concentration.

Calculate the dye content of the specimen as follows:

$$\text{Percent dye conforming to MIL-D-3668} = \frac{100C_a}{P_a\ C}$$

$$\text{Percent dye conforming to MIL-D-3284} = \frac{100C_b}{P_b\ C}$$

where: C_a = Concentration calculated above,
C_b = Concentration calculated above,
C = Concentration of specimen in grams per liter,
P_a = Original percent purity of dye conforming to MIL-D-3668 prior to blending, and
P_b = Original percent purity of dye conforming to MIL-D-3284 prior to blending.

4.2.4.2 Volatile matter. Weigh to the nearest milligram approximately 5 g of the specimen in a tared, glass-stoppered weighing bottle. Remove the stopper and dry to constant weight at 70° to 75° C. Cool to room temperature in a desiccator and weigh. Calculate the percent volatile matter as follows:

$$\text{Percent volatile matter} = \frac{100(A - B)}{W}$$

where: A = Weight of specimen and stoppered bottle before heating in grams,
B = Weight of specimen and stoppered bottle after heating in grams, and
W = Weight of specimen in grams.

4.2.4.3 Particle size. Use sieves conforming to RR-S-366. Nest the sieves in order of decreasing mesh size (with the sieve of largest mesh on top) on a receiving pan. Weigh to the nearest 0.1 g approximately 10 g of the specimen and then use one of the following procedures:

(a) Dry method. Place the weighed specimen on the top sieve and brush the material with a camel's-hair brush until no more specimen passes through the sieve. Remove the sieve and weigh the material retained. Repeat this procedure with each of the other sieves. Calculate the percent material passing through each sieve.

(b) Wet method. Mix the weighed specimen with sufficient water in a beaker by stirring with a glass rod to produce a smooth paste. Carefully wash the thoroughly wetted specimen through the

sieves. (The use of a wetting agent is permitted.) Dry the sieves in an oven at 70° to 75° C and weigh the material remaining on each sieve. Calculate the percent material passing through each sieve.

4.2.4.4 Apparent density. Determine apparent density in accordance with ASTM D1895, method A.

5. PREPARATION FOR DELIVERY

5.1 Packing. Packing shall be level B or C as specified (see 6.2).

5.1.1 Level B. Uniform quantities of no less than 150 and no more than 300 pounds ± 1/4 percent of the marked net weight of dye shall be packed in a fiber drum conforming to rule 51, section 2 of the Uniform Freight Classification for a weight limit of over 225 but not over 300 pounds, with an aluminum barrier of 0.5 mil minimum thickness incorporated into one of the inner plies of the sidewall. Each drum shall be provided with a close fitting bag liner formed from polyethylene of 4 mils minimum thickness conforming to type I, grade and finish optional of L-P-378. Seams shall be completely heat sealed and shall meet the heat-seal strength requirements of L-P-378. The filled bag shall be closed by heat sealing, tying, or knotting. A minimum of eight units of desiccant conforming to MIL-D-3464 shall be placed on top of the closed liner. Drum closure shall be fully gasketed and shall form a tight seal between the rim and the top of the drum.

5.1.2 Level C. Uniform quantities of no less than 150 and no more than 300 pounds ± 1/4 percent of the marked net weight of dye shall be packed in containers which comply with the Uniform Freight Classification Rules, the National Motor Freight Classification Rules, or other carrier rules as applicable to the mode of transportation. Containers shall be capable of being stacked and of supporting superimposed loads during shipment and shall assure safe delivery to destination without damage to contents. Containers shall be acceptable for shipment at the most favorable rate of the applicable regulation provided that all requirements specified herein have been met.

5.2 Marking. Marking shall be in accordance with MIL-STD-129. In addition, each container shall be durably and legibly marked with contrasting letters and background to show the net weight of contents and the following information:

CAUTION

Avoid skin contact.
Avoid breathing dust or fumes.
Use with adequate ventilation.

6. NOTES

6.1 Intended use. Dye Mix, Violet is intended for use in the manufacture of violet signaling smoke mixtures.

6.2 Ordering data. Procurement documents should specify the following:

(a) Title, number, and date of this specification.
(b) Level of packing required (see 5.1).

6.3 Batch. A batch is defined as that quantity of material which has been manufactured by some unit chemical process or subjected to some physical mixing operation intended to make the final product substantially uniform.

6.4 Dyes of known purity. Dyes of known purity conforming to MIL-D-3668 and MIL-D-3284, respectively, may be obtained from Commanding Officer, Edgewood Arsenal, Quality Assurance Directorate, Edgewood Arsenal, Maryland 21010.

6.5 Significant places. For the purpose of determining conformance with this specification, an observed or calculated value should be rounded off "to the nearest unit" in the last right-hand place of figures used in expressing the limiting value, in accordance with the rounding-off method of the Recommended Practices for Designating Significant Places in Specified Limiting Values (ASTM E29).

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Army - MU
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Review activities:

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